PB 200 846

Air Pollution Aspects of Emission Sources

NITRIC ACID MANUFACTURING

A Bibliography with Abstracts

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AIR POLLUTION ASPECTS OF EMISSION SOURCES: NITRIC ACID MANUFACTURING— A BIBLIOGRAPHY WITH ABSTRACTS

Office of Technical Information and Publications
Air Pollution Technical Information Center

ENVIRONMENTAL PROTECTION AGENCY
Air Pollution Control Office
Research Triangle Park, North Carolina
May 1971

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Stock Number 5501-0043

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Air Pollution Control Office Publication AP-93

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AP-93, Air Pollution Aspects of Emission Sources:
Nitric Acid Manufacturing – A Bibliography with Abstracts

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AIR POLLUTION ASPECTS OF EMISSION SOURCES: NITRIC ACID MANUFACTURING — A BIBLIOGRAPHY WITH ABSTRACTS

INTRODUCTION

Nitric acid manufacturing contributes significantly to the overall air pollution level in the United States. To aid efforts to improve air quality, the Air Pollution Technical Information Center (APTIC) of the Office of Technical Information and Publications, Air Pollution Control Office, has compiled this bibliography relevant to the problem and its solution.

Approximately 81 abstracts have been selectively screened from the contents of APTIC's information storage and retrieval system to cover the 14 categories set forth in the table of contents. The compilation is intended to be representative of available literature, and no claim is made to all-inclusiveness.

Subject and author indexes refer to the abstracts by category letter and APTIC accession number. Generally, higher accession numbers, representing the latest acquisitions, cover the most recent material.

All documents abstracted herein are currently on file at the Air Pollution Technical Information Center, Air Pollution Control Office, Environmental Protection Agency, P. O. Box 12055, Research Triangle Park, North Carolina 27709. Readers outside the Environmental Protection Agency may seek duplicates of documents directly from libraries, publishers, or authors.

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A. EMISSION SOURCES

01583

R.W. Gerstle R.F. Peterson

ATMOSPHERIC EMISSIONS FROM NITRIC ACID MANUFACTURING PROCESSES - A COMPREHENSIVE SUMMARY. Preprint. (For Presentation at the American Inst. of Chemical Engineers, Detroit, Mich., Dec. 8, 1966.)

Atmospheric emissions from nitric acid plants depend on plant operating conditions, production rates, and the use of control devices. Data in this article show that plants operating within design capacities and producing 55-60% nitric acid can limit the nitrogen oxides concentration to 0.3% in the stream leaving the absorption tower. This is equivalent to about 50 pounds of nitrogen oxides per ton of nitric acid (100% basis) produced. Installation of scrubbers or catalytic reduction equipment can reduce these emissions by 50 to 97%. Emissions during startup or shutdown usually do not create any special problems. (Author summary modified)

13698

Mohrenheim, Anton F.

AIR POLLUTION AND THE METAL FINISHING INDUSTRY. Plating, March 1969.

The role of nitrogen oxides in air pollution is discussed in order to inform those who work with nitric acid and aqua regia of their capacity for creating or preventing air pollution. Nitrogen dioxide itself is toxic and, in addition, contributes to chemical smog production through a photochemical chain reaction. Even though the metal manufacturing and finishing industry uses larger quantities of nitric acid than the precious metal industry, the latter may release comparible amounts of nitrogen dioxide. This is demonstrated by the quantitative reaction of gold and nitric acid. In the precious metal industry, closed systems should be used with only stoichiometric amounts of aqua regia. For pickling and similar work in the metal manufacturing and finishing industry, mist collectors or air scrubbers should be used.

16699

British Oxygen Co. Ltd., Glasgow, Scotland

CURRENT METHODS OF COMMERCIAL PRODUCTION OF NITROUS OXIDE. APPENDIX 1. Brit. J. Anaesthesia, vol. 39:440-442, May 1967.

Nitrous oxide is produced on a commercial scale by passing an ammonium nitrate solution through a primary scrubbing tower to a gas-heated reactor. As decomposition takes place, nitrous oxide leaves the reactor, together with steam, ammonia, nitric acid, nitrogen, and traces of nitric oxide and nitrogen dioxide. Initial cooling of the merging gases causes most of the ammonia and nitric acid to revert to ammonium nitrate, which is returned to the reactor. Residual ammonia and nitric acid are removed by a water scrubber; higher oxides, by caustic/permanganate scrubber; and ammonia traces, by an acid scrubber. When free of all impurities except moisture and nitrogen, the gas is compressed and dried in an alumina drier battery. The dry, compressed gas is next liquefied to release nitrogen and evaporate pure nitrous oxide. The evaporated nitrous oxide is then compressed to cylinder pressure and passed through a second alumina drier battery to a cylinder filling line. In purity tests for nitric oxide and nitrogen dioxide determination, the gas leaving each drier is passed through a visual bubbler containing an acid potassium permanganate solution and a Saltzman reagent. An alarm is automatically sounded if nitric oxide and nitrogen dioxide concentrations reach 1 vpm.

17076

Belaga, M. B. and P. N. Maystruk

SANITARY PROTECTION OF AIR IN VINNITSA. U.S.S.R. Literature on Air Pollution and Related Occupational Diseases, vol. 8:241-246, 1963. (B. S. Levine, ed.) (Also: Gigiena i Sanitariya, 26(1):73-76, 1961. CFSTI: 63-11570)

Plans are presented for the purification of discharges from different shops and departments of a superphosphate plant which currently emits 10.5 tons of sulfur dioxide, 6.5 tons of nitric acid, 1.2 tons of sulfuric acid, 0.5 tons of fluorides, and one ton of superphosphate and tricalcium dust each day. Even at a distance of 2000 meters from the plant, the maximum fluorine concentrations are 13 times in excess of the allowable limit. Similarly, sulfur dioxide concentrations at 1000 meters and sulfuric acid aerosols at 500 meters have been found to exceed allowable limits. The maximum concentration of dust at 200 m from the plant is 15.4 mg/cum, or thirty times in excess of the allowable limit. Dust samples collected at 200-1000 meters from the plant showed a fluorine content of 0.8 to 1.4%. Soil samples at 200, 500, and 1000 meters contained 16.9, 9.61, and 8.7 mg of fluorine per 100 g of soil. Among the measures being taken to reduce pollution are the elimination of gas leaks by equipment hermetization, the installation of dust catching and gas purification equipment, and the construction of high stacks for greater dispersion of pollutants. It is further recommended that the sulfuric acid department build a separate housing for its exhaust fans, use filters to raise tail-gas utilization efficiency, and build a warehouse to store the apatite concentration.

18305

Lindau, L.

AIR POLLUTION AND THE MANUFACTURE OF INORGANIC CHEMICALS. (Luftfororening vid framstallning av oorganiska baskemikalier.) Text in Swedish. Statens Naturvardsverk, Stockholm, Publikationer No. 4, 66p., 10 refs.

The investigation deals with air pollution problems in connection with the manufacture of basic inorganic chemicals such as sulphuric acid, hydrochloric acid, phosphoric acid, ammonia, nitric acid, chlorine and sodium hydroxide. The report contains a survey of present conditions, an analysis of various technical methods to reduce the emissions, and a discussion of the economic consequences of these methods. The purpose of the survey is to supply information to the Swedish authorities dealing with air pollution control. The rates of emission from the chemical plants are described as kg/ton product. The costs of air pollution abatement vary. In certain cases, e.g., the recovery of sulphur in connection with the production of am-

manna, the necessary investments can be written off. In other cases, e.g., introduction of the double-contact process for the manufacture of sulphuric acid, the increasing yield can only partially motivate the investments required. There are also cases when the costs entirely belong to the air pollution account. A comparison between Swedish and foreign plants indicates that emissions are of the same magnitude. Essential improvements are possible to obtain in new plants and the latest Swedish production units have applied this to a great extent.

21284

Hals, Finn A.

ENVIRONMESTAL POLLUTION CONTROL THROUGH MHD POWER GENERATION. Combustion, 41(11):27-29, May 1970.

In addition to offering advances in power technology of significant benefit to society, magnetohydrodynamics (MHD) shows promise of solving serious air and thermal pollution problems faced by steam-electric power plants. The use of MHD-steam power plant could significantly reduce thermal pollution of water since, due to higher efficiencies, less than half the amount of cooling water used by conventional fossil-fueled steam power plants would be required. Since the supplemental steam turbine can be replaced with a supplemental gas turbine, MHD generators can be designed to reject all heat into the atmosphere and none to water. With no cooling water necessary, MHD generators can be located in water-poor but fuel-rich areas, opening them to industrialization. Particulate emission would be controlled by careful electrostatic precipitation, since the economic operation of the plant requires the recovery of an alkali seed impurity added to enhance electrical conductivity of the combustion gases. Particulate removal in excess of 99% is, therefore ensured. The temperatures at which MHD generators operate make the recovery of nitrogen oxides and sulfur oxides in the form of nitric and sulfuric acid technically feasible and economically attractive.

22877

Stuttgart Univ. (West Germany). Inst. fuer Verfahrenstechnik und Dampfkesselwesen

KEEPING THE AIR PURE. (Reinhaltung der Luft). 58p., 1968. 25 refs. Translated from German. Belov and Associates, Denver, Colo., 80p., Feb. 5, 1970.

A review of technical articles relating to air pollution is presented. Sampling techniques and statistical evaluation of results are discussed. The effects of gaseous impurities on humans and plants are briefly mentioned. Maximum emission values for nitric oxide, nitric acid, chlorine, hydrogen chloride, hydrogen sulfide, and sulfur dioxide are tabulated. Measurement methods, including filters, absorption bottles, and various continuous methods are described. SO2 is generally measured by the silica gel method, the West Gaeke method, the 'Ultragas 3' method, the Pico-flex instrument, or by infrared spectrophotometry. Isopropanol is a good absorption medium for sulfur trioxide. Dewpoint measurement and detectors are mentioned. NO2 can be measured by the Saltzman method, and by photometric or colorimetric means. Measurement of H2S and fluorine emissions may be done by the sodium hydroxide method. Methods for carbon monoxide and dioxide are mentioned. Organic compounds are measured by gas chromatography. Methods for measuring and counting dust contaminants, and stack sampling are discussed. Optical and electrostatic methods of determining smoke shade are described. The Konimeter, impinger, and dust fall methods are considered. A discussion of plume behavior, including stack height, turbulence, diffusion, and winds, is presented. Several laws regarding emissions are mentioned.

26226

Perrine, Richard L., and Limin Hsueh

POWER AND INDUSTRY: CONTROL OF NITROGEN OXIDE EMISSIONS. In: Project Clean Air, California Univ., Berkeley, Task Force 5, Vol. 1, Section 9, 11p., Sept. 1, 1970. 32 refs.

When fossil fuels are burned with air some of the nitrogen reacts with oxygen forming nitrogen oxides; the major source of emissions of NOx in California is motor vehicles, but stationary power sources and others also contribute large quantities. The higher the peak combustion temperature the more nitric oxide is formed. Most current efforts to deal with the problem are centered on developing improved combustion processes and on the design of the burner and type of firing. Some improvement may be obtained through combustion process modifications, but these are constrained by existing designs, stable operating requirements, and adverse secondary effects. Some basic approaches which have been developed for removal of NOx emissions from nitric acid plant stack gases include catalytic decomposition, catalytic reduction, absorption on solids, and caustic scrubbing. A number of modifications to operating conditions or burner design include low excess air combustion, flue gas recirculation, steam and water injection, burner configuration, and fluidized bed composition. The complex interaction of mixing, heat transfer, fluid mechanics, and chemical kinetics within the burner needs to be understood. Simplified models of the combustion process are necessary to aid in the understanding of the critical processes controlling nitric oxide formation and to provide a means for the systematic analysis of cause-effect relationships.

B. CONTROL METHODS

00587

J.A. Brink, Jr., W.F. Burggrabe, L.F. Greenwell

MIST REMOVAL FROM COMPRESSED GASES. Chem. Eng. Progr., 62(4):60-66, April 1966.

Fiber mist eliminators have been successfully used to purify gases and solve difficult air pollution problems involving methanol synthesis gas, sulfonation and chlorination process gases, nitric acid process gases, chlorine, and compressed air. Extensive research and development work resulted in the development of fiber mist eliminators for the collection of submicron mist particles. The first plant-scale installations were made for the control of air pollution from sulfuric and phosphoric acid plants. After full-scale units had been proven highly efficient on stack gases containing submicron particles, further research was undertaken to develop *fiber* mist eliminators which would be most economical for the collection of particles which are predominantly 1 to 20 microns in diameter. The installation of fiber mist eliminators within various processes to purify gases was started after several difficult air pollution problems had been solved. The widespread application of fiber units to chlorine plants was reported in detail, but the applications to many other processes has not been reported previously. It should be noted that mists are present in many chemical processes at pressures ranging up to 5,500 lb./sq. in. gauge. The temperatures at which mists are present are usually moderate since many mists vaporize at higher temperatures.

00959

B. B. Sundaresan, C. I. Harding, F. P. May, and E. R. Hendrickson

A DRY PROCESS FOR THE REMOVAL OF NITROGEN OXIDES FROM WASTE GAS STREAMS IN NITRIC ACID MANUFACTURE. Preprint. (Presented at the 59th Annual Meeting, Air Pollution Control Association, San Francisco, Calif., June 20-25, 1966, Paper 66-96.)

Experimental studies were conducted using a commercial zeolite to remove NOx from waste gas streams in a nitric acid plant. NOx retained in the bed was recovered as enriched NOx and HNO3 by regenerating the bed at elevated temperatures with hot air and/or steam. Test results indicate that such a system could be incorporated into an existing nitric acid plant, thereby eliminating release of significant quantities of NOx into atmosphere. The conclusions are enumerated below: (1) A process to remove NOx from the waste gas streams of nitric acid plants has been found; (2) Complete NOx removal as proved by this system will eliminate release of NOx into the atmosphere; (3) Commercial zeolite used in this process can remove NOx along with most of the moisture present in the tail gas; (4) NOx and H2O retained in the bed has been recovered as enriched NOx and HNO3 for possible feedback into the process stream; (5) It has been estimated that in a 300 ton acid plant by feeding back the recovered NOx into the process stream, about 4 to 5 tons per day of 60% HNO3 now being wasted could be added to production; and (6) The increased production should offset the additional investment for such a system, making the process economically feasible. (Author summary and conclusions)

01125

D. Zanon and D. Sordelli

PRACTICAL SOLUTIONS OF AIR POLLUTION PROBLEMS FROM CHEMICAL PROCESSES. (Realizzazioni nel Campo della Prevenzione dell' inquinamento Atmosferico di Origine Industriale.) Translated from Italian. Chim. Ind. (Milan), 48(2):251-261, March 1966.

A strict control of pollutant to be dispersed in the atmosphere offers technical and economic problems, both in the design and the operation of chemical processing units. Three examples of processes for which pollution control has been established are described: SO2 derived from contact sulfuric acid and from hydroxylamine sulfate plants, nitrous gas from low and high-pressure nitric acid plants, and fluorine-containing effluents from hydrogen fluoride production. The general approach, kind of abatement process adopted, materials and construction costs are discussed.

02051

J. Feist.

THE CATALYTIC REDUCTION OF NITROUS GASES DURING THE MANUFACTURE OF NITRIC ACID. Die Katalytische Reduktion Von Nitrosen Abgasen Bei Der Erzeugung Von Salpetersaure. Proc. (Part I) Intern. Clean Air Cong., London, 1966. (Paper VI/15), pp. 199-202.

Discusses a catalytic reduction process for reducing nitric oxide present in the waste gas from nitric acid for manufacture to a concentration of 100 ppm. Flow sheets illustrate thermal integration of the catalytic process with the overall process. Discusses the use of metal and ceramic catalysts. (Author abstract)

04658

R. W. Bayley

DESORPTION OF WASTE WATER GASES IN AIR (PART I). Effluent Water Treat. J. (London) 7, (2) 78-84, Feb. 1967.

The air stripping of volatile or gaseous polluting constituents from industrial waste waters in desorption units is used for pretreatment of the waste prior to discharge to a public sewer or stream. Where an air-pollution problem exists, the desorbed gas must be dispersed by stacks or the desorbed constituent recovered. The design of such desorbing units based on known chemical engineering principles is illustrated by examples of the removal of the cyanide from the effluent of a gas plant and ammonia from the effluent from a nitric acid plant. The desorption unit may use either diffused air bubbles passing through the liquid or counter-current towers packed with Rasching rings.

05151

B. A. Kerns

CHEMICAL SUPPRESSION OF NITROGEN OXIDES. Westinghouse Electric Corp., Pittsburgh, Pa., Headquarters Mfg. Lab. (1964). 6 pp.

An approach to NO and NO2 fume control by eliminating the fumes before their release from pickling, milling and bright dipping solutions was investigated. Since classical chemistry shows a reaction between most primary amines and the oxides of nitrogen, a study of an available, inexpensive, and readily adaptable amide, urea, was undertaken. The investigations included a thorough study of the urea-nitric acid-nitrogen oxides reactions for both copper and iron-68 analyses of the urea (for purity), and of the evolved gases, and the effect of the urea nitric acid system on the various types of stainless steels and other metals which could be employed. A thorough study of the possible hazards of the urea-nitric acid system was undertaken also. In the case of chemical milling urea successfully lowered the NO2 fumes to almost undetectable levels, but this treatment did not suppress the HNO3 vapors which coincidentally are released from these hot chemical milling solutions. Thus a small water scrubbing apparatus is still required to prevent these vapors from being released to the atmosphere. The use of a HNO3-urea solution system produces a satin finish in less than half of the time now required to bright dip and release no toxic fumes to the atmosphere.

05369

F. C. Betz and H. J. Feist

CATALYTIC AFTERBURNING OF ORGANIC AIR POLLUTANTS. Technik (Berlin) 20 (6), 395-400 (June 1965). Ger. (Tr.)

Newly developed all-metal catalysts are discussed which are designed on the basis of the building block assembly system; in practice, they achieve an average running time of 25,000-35,000 working hours. A catalyst, which speeds up a reaction because of its presence, without itself participating in the reaction, reduces the decomposition temperature during combustion. A reaction temperature of 250-350 C was achieved with all-metal catalysts developed for catalytic exhaust gas purification. The cold exhaust gases flow through a heat exchanger and are preheated. Then they are heated by means of oil burners, gas burners, or electrical heating elements until they reach the catalytic reaction temperature. A fan then moves the exhaust gases to the catalyst where the irritants are oxidized. The heat released during catalytic combustion is largely recovered in the heat exchanger and it is used for heating the cold exhaust gases as combustion here is exothermal. At a reaction temperature of about 250-350 C, all combustible components are oxidized in the exhaust gas. As a result of the temperature increase in the exhaust gas in the catalyst, the positive heat change of this reaction can measured which gives a figure directly proportional to the irritant concentration. The catalytic exhaust gas purification unit thus serves as a measurement instrument for the concentration of the exhaust gas. A measurement system used for continual surveillance is presented in diagram. Applications of catalytic afterburning are discussed in relation to the following: drying and hardening processes, phthalic acid and maleic acid anhydride production, nitric acid production, NO/NO2 reduction.

05401

ATMOSPHERIC EMISSIONS FROM NITRIC ACID MANUFACTURING PROCESSES. Public Health Service, Cincinnati, Ohio, Div. of Air Pollution and Manufacturing Chemists Association, Washington, D.C. 1966. 96 pp. (999-AP-27.)

Emissions to the atmosphere from the manufacture of nitric acid were investigated jointly by the Manufacturing Chemists' Assoc., Inc. and the U.S.P.H.S.; the study was the second in a cooperative program for evaluation of emissions from selected chemical manufacturing processes. The report describes the growth and potential of the nitric acid industry, the principal processes for production of nitric acid, process variables, emissions from plants under normal operating conditions, and the methods and devices used to limit and control emissions. The sampling and analytical techniques by which emissions were assessed are presented in detail. (Author's abstract)

06123

O. Jeitner, and K. Konig

ELIMINATION OF NITROUS GAS EMISSION BY CATALYTIC REDUCTION. Beseitigung der Nitrosegasemission durch katalytische Reduction. Chem. Tech. (Berlin) 19, (3), 166-9, Mar. 1967. Ger.

At the nitric acid plant in Piesteritz, East Germany, NO in the waste gas was to be catalytically reduced by hydrogen. The hydrogen was a by-product and contained 0.1% by volume of H2S and 0.05% by volume of PH3, both toxic to the Pd catalyst used. Therefore, the hydrogen had to be washed by passing it through two washing towers containing 30% HNO3. One tower also contained 15% NaOH and the other water. Complete elimination of the NO was possible using 0.4 to 0.6% more hydrogen than the stoichiometrically required volume. If the flow of hydrogen through the catalyst is closely controlled, the resulting nitrogen is virtually free of oxygen and hydrogen.

06844

H. C. Anderson, P. L. Romeo and W. J. Green

A NEW FAMILY OF CATALYSTS FOR NITRIC ACID TAIL GASES. Engelhard Ind. Tech. Bull. 7 (3), 100-5 (Dec. 1966).

The palladium unitory ceramic catalyst remove oxides of nitrogen from tail gases produced during the production of nitric acid was evaluated. The new catalyst, provides excellent abatement at 100 p.s.i.g., using space velocities of 10l,000. Even at 150,000, 94% of the NOx was removed, with ammonia in only slight excess over the NOx. Bench-scale and field experience have shown that the unitary ceramic catalyst is well adapted to the treatment of nitric acid stack gases.

07093

REVIEW OF RESTRICTING GAS EMISSION FROM NITRIC-ACID PLANTS. ((VDI (Verein Deutscher Ingenieure) Kommission Reinhaltung der Luft, Duesseldorf, Germany.)) (VDI No. 2295.) (July 1963) Ger. (Tr.) 12 pp.

The control of nitrogen oxides during the production of nitric acid was discussed. Nitrogen oxides emissions are restricted by absorption, suitable discharge outlets, and on the basis of imissions. Because of the particularities of nitrous gases, the content of the waste gases cannot be completely controlled.

07535

W. Leisbe

CLEAN AIR MAINTENANCE - AN IMPORTANT TASK FOR CHEMISTRY AND ECONOMY. (Reinhaltung der Luft - ein dringendes Anliegen fur Chemie und Wirtschaft.) Text in German. Allgem. Prakt. Chem. (Vienna), 18(8):239-241, Sept. 10-17, 1967. 4 refs.

This article is a summary of two lectures given at meetings of chemical societies. The problem of air pollution and some control methods are outlined. Typical examples of well-known air pollution problems are mentioned: London's smog chiefly caused by domestic heating, the smog of Los Angeles due to automobiles, the sun, and temperature inversions, and the industrial air pollution of the Ruhr Valley. Some characteristic data for all three examples are quoted. The techniques for the control of dust emissions are farthest advanced. This is

verified by the fact that in Germany, emission of cement dusts decreased to one third while the production of cement tripled in the last 17 years. Far less satisfactory is the control of SO2 emissions. About twice as much sulfur is blown into the air than is used for the production of sulfuric acid. Some wet and dry processes for the elimination of SO2 from smoke are mentioned, but no method is known today which is both effective and economical. The chemical industry tackled its problems mostly by reducing the emission of air polluting substances by increasing the efficiencies of the relevant chemical processes. Examples are the production of sulfuric acid and nitric acid. Organic compounds can be recovered by either absorption on activated charcoal or oxidation by catalytic afterburners.

07552

Billings, Charles E., Charles Kurker, Jr., and Leslie Silverman

SIMULTANEOUS REMOVAL OF ACID GASES, MISTS, AND FUMES WITH MINERAL WOOL FILTERS. J. Air Pollution Control Assoc., 8(3):195-202, Nov. 1958. 20 refs. (Presented at the 51st Annual Meeting, Air Pollution Control Assoc., Philadelphia, Pa., May 26-29, 1958.)

Investigations have indicated that two in. thick filters at four lb/cu. ft. packing density will remove up to 80% of acid mist and up to 99% of acid gases and fumes. Total filter life depends upon concentration of contaminant in the entering air. A summary of filter performance is given. Estimated operating life based upon one use of the filter material can be obtained from the data given. With particulates such as iron oxide and fly ash, it has been found possible to wash and reuse filters about ten times. When iron oxide was collected simultaneously with SO2, filters were reused about eight times. Acid gas collection is significantly improved by the presence of moisture on slag wool filters. Mineral wool filters have several features such as, low cost (about 1 cents/lg.), small fiber diameter (4 micron and ability to withstand high temperatures (1000 deg F.). Slag wool will simultaneously remove sub-micron particulate materials with 9?% to 99% efficiency. Resistance to flow through two in. slag wool filters (with an HF efficiency of 95%) is on the order of one or two in. of water, or if continuously moistened, at most 6 in. of water.

09773

FAN SCRUBBER HALTS CORROSION ENDING NEED FOR ROOF REPAIRS. Chem. Process., 31(4):67, April 1968.

The manner in which escaping acid fumes were controlled at a particular plant is described. An existing system of water scrubbers was supplanted by a separator based on a centrifugal fan. Flow through the separator is 14,000 cfm of an exhaust containing 750 ppm of nitric acid and nitrogen oxides and 350 ppm of hydrofluoric acid. Most of the fumes are separated by centrifugal force in the fan, into which 6 gpm of water is sprayed. The partially cleaned exhaust then passes through a 48 x 80 x 6 in thick polypropylene filter which removes nearly all of the remaining wetted fumes. Fumes leaving the separator were reduced to trace amounts. Scrubbing water requirements were reduced by 34 gpm. The complete system was installed at a cost of $8100, less than $.70 cfm.

09981

Tikhonenko, A. D. and M. N. Nabiev

NATURAL-GAS CATALYTIC REDUCTION OF NITRIC OXIDE TAIL GASES FROM NITRIC ACID PRODUCTION. Translated from Russian. Uzbesk. Khim. Zh., 11(4):6-9, 1967. 2 refs. CFSTI: PB 178106T

The catalytic reduction of nitrogen oxides is the most progressive means of purifying tail gas from nitric acid production. The process of catalytic reduction of nitric oxides by methane in the form of natural gas at atmospheric pressure with the use of platinized nickel-chromium foil and a two-layer catalyzer is described. In operation over 710 hrs, the nickel-chromium foil showed sufficient thermal stability under conditions assuring complete purification of the gas; catalyst activity significantly decreased and was reduced with H2 at 320 deg. C. The conditions for complete nitric oxide reduction were found and also those for achieving the sanitary norm of NO+NO2 content (0.02 percent). In a two-layer catalyst it was possible to decrease the temperature of the gas entering the catalyzer to 450 deg. and the resulting CH4:O2 ratio was 0.8.

10017

Bloomfield, Bernard D.

CONTROL OF GASEOUS POLLUTANTS. Heating, Piping, Air Conditioning, 40(1):195-200, Jan. 1968. 26 refs.

Control technology in relation to air pollution involves the application, singly or in combination, of tall stacks for dispersion, process changes, and control equipment. Most gaseous contaminants can be controlled using the techniques of absorption, adsorption, direct flame combustion, and catalytic combustion. The theoretical principles of design and operation preclude under most circumstances the use of any of the shelf items for air pollution control purpose. Good design, construction, and proper operation are the requisites of a satisfactory system. The special characteristics of a number systems are described. A table of selected air quality standards is given for such pollutants as SOx, NOx, CO, H2S, and ozone.

10159

Atroshchenko, V. I., and E. G. Sedasnova

RATE OF NITROGEN OXIDES ABSORPTION BY ALKALINE SOLUTIONS AND NITRIC ACID. Zh. Prikl. Khim., 25(11):1143-1150, 1952. 13 refs. Translated from Russian by B. S. Levine, U. S. S. R. Literature on Air Pollution and Related Occupational Diseases, Vol. 6, 299p., April 1961. CFSTI: TT 61-21982

The absorption of nitrogen oxides by alkaline solutions has become economically advantageous to the nitric acid industry. In connection with the complex processes which take place in the formation of nitric acid and alkaline nitrates from nitric oxide, an experimental study was made of the relative velocity of the total nitric oxide conversion at different ratios between acid and alkaline absorption. The results of the study demonstrated that a functional relationship existed between the degree of nitrogen oxides absorption and the increase in the specific gravity of alkaline absorbers, accompanied by a corresponding reduction in the degree of nitric acid absorption. The results also established that at the combined production of nitric acid and sodium nitrate by the method of increasing the degree of nitrogen oxides absorption by alkaline solution, the reaction volume can be reduced considerably.

11058

W. Teske

IMPROVEMENTS IN THE PROCESSES AND OPERATION OF PLANTS IN THE CHEMICAL INDUSTRY LEADING TO REDUCED EMISSION. Staub (English translation), 28(3):25-33, March 1968. CFSTI: TT 68-50448/3

The emissions from chemical plants can be reduced, in special cases, by changing the production process or, in general, by using a gas cleaning method. Change in the production process

may be achieved by a basic alteration of the process itself, by changing the mode of operation, by modifying the equipment and by using a different raw material. For this purpose, the double-contact method for sulphuric acid production, the pressure method for nitric acid recovery and the introduction of a covered carbide furnace are mentioned as examples. The superphosphate process, viscose process, production of betanaphthol, production of thermal phosphoric acid and production of calcium chloride are given as examples for waste gas cleaning. (Author's summary)

11549

Bingham, E. C. Jr.

NITRIC ACID PLANT'S CATALYTIC BURNER PREVENTS TAIL GAS STREAM AIR POLLUTION. Preprint, Farmers Chemical Association, Inc., Tyner, Tenn., 3p., 1968.

Air contamination is prevented from a ton per day nitric acid manufacturing plant by passing the tail gas through a catalytic burner which reduces residual oxides of nitrogen into a colorless stream. After purification in the combustion chamber, which contain a catalyst charge, the exhaust stream can be safety directed to a turbine expander for power recovery to assist in driving the main compressor of the acid manufacturing unit. The catalytic reaction also increases the life of the expander because the afterburner exhaust stream has no nitric acid carry over that could eventually strip out the turbine blades. Tests conducted during the first six months of operation of the charge showed a cleaning of NO2 pollutants ranging between 95 and 98 percent. The unit maintained the high rate of reduction of fumes while operating at space velocities in the order of 120,000 cubic feet of gas per cubic foot of catalyst system per hour.

12637

W. Teske

EMISSIONS AND ABATEMENT OF OXIDES OF NITROGEN IN NITRIC ACID MANUFACTURE. Chem. Eng., No. 221, CE263-266, Sept. 1968.

The emission problem in the manufacture of nitric acid results from incomplete conversion of nitrous oxide to nitric acid. Some of the processes for reducing the emissions which are discussed briefly include: Alkaline absorption with milk of lime or aqueous ammonia; oxidation with hydrogen peroxide or ozone; absorption in an aqueous solution of magnesium oxide; removal as nitrosylsulfuric acid by treatment with a sulfuric acid, nitric acid mixture; and catalytic reduction processes.

13202

Schmitt, Karl, Wilhelm Ester, Hans Heumann, and Harry Pauling

NITROGEN OXIDE CONVERSION. (Hibernia Chemie GmbH, Gelsenkirchen-Buer, Germany, and Harry Pauling, Munich, Germany) U. S. Pat. 3,453,071. 7p., July 1, 1969. 4 refs. (Appl. May 16, 1966, 29 claims)

In the production of nitric acid and other nitrogenous products, exhaust gas is produced which contains significant quantities of nitrogen oxides, particularly NO and NO2. A process for absorbing these oxides and recovering them as ammonium nitrite includes adjusting the mole ratio of NO to NO2 to 1 and then introducing the adjusted gas into an ammoniacal solution of ammonium nitrate. The ammonium nitrate content of the absorbent solution is controlled so that the solution viscosity at any given temperature is higher than the viscosity of water at the same temperature. When the ammonium nitrate concentration is maintained at about 40 to 50 weight percent and the absorption process is operated at 20 to 30 C, at least half the ammonium nitrite formation takes place at the liquid-vapor interface. The remainder of the ammonium nitrite is produced in the gas phase by successive absorption of small amounts of gaseous ammonia in the vapor space, where it is neutralized with water vapor and nitrogen oxide to form ammonium nitrates as well as the ammonium nitrites. These dissolve in the absorbent solution. By preventing the development of easily decomposable ammonium nitrite mists, the process minimizes efficiency losses and explosion dangers.

13205

Markvart, Miroslav and Vladimir Pour

SELECTIVE REDUCTION OF NITROGEN OXIDES WITH AMMONIA. (Selektivni redukce kyslicniku dusiku amoniakem). Text in Czech. Chem. Prumysl (Prague), 19(1):8-12, 1969. 12 refs.

In manufacturing nitrogen acids, catalytic reduction of nitrogen oxides in fall gases is the most effective method of neutralization. Using ammonia as a catalyst, nitrogen oxides can be selectively eliminated. The consumption of fuel using ammonia is approximately ten times lower than with other reducers. Tests were conducted to gain more information about the method. All measurements were taken under atmospheric pressure, and the reaction took place in the kinetic range. Nitrogen oxides were detected by the standard titrimetric method. Catalyzers were prepared by depositing active metal on aluminium. In the absence of oxygen, the reduction is fastest on platinum catalyzers; 99% conversion is reached with temperatures above C. In the presence of oxygen on the same catalyzer, the temperature may be as low as 180 C. The increase in speed of reaction is most evident with small concentrations. The activity of the catalyzer is greatest when the amount of Pt is 1%. In all of the tests, the greater the speed of the gases, the higher the temperature must be. The only disadvantage of this method is that ammonic salts are generated that may deposit on the cool parts of the reactor.

13689

Atroshchenko, V. I., A. N. Tsvetlin, A. P. Zaporin, and V. S. Zolotarev

UTILIZATION OF NITROGEN OXIDES - BY-PRODUCTS OF CERTAIN INDUSTRIES. (Utilizatsiya okislov azota - otkhodov nekotorykh proizvodstv). Text in Russian. Khim. Prom. (Moscow), 1(1):79-80, 1960.

Production of nitric acid from exhaust gas with high NO content as compared with exhaust gas with low NO content *plus* NO2 is discussed. A method is described which involves cooling the gases to 25-30 C, introducing additional air, and carrying out oxidation in a cooler-oxidizer. About 8% absorption is achieved with 35% nitric acid absorbent. Specifications for an operating installation which produces 2500 kg of 55% acid are given. A modified version using oxygen rather than air is mentioned.

13893

Anderson, H. C., P. L. Romeo, and W. J. Green

A NEW FAMILY OF CATALYSTS FOR NITRIC ACID TAIL GASES. Nitrogen, no. 50:33-36, Nov./Dec. 1967. 6 refs.

A unitary ceramic cartridge was designed to act as a precious metal catalyst support. The support consists of a block of ceramic, through which a multitude of small parallel channels pass which are coated with the precious metal. Bench-scale and field experience have shown that the unitary catalyst is

well-adapted to the treatment of nitric acid stack gases. Using natural gas as a fuel, decolorization of stack gases is effected using palladium as the catalyst on the ceramic support. The ceramic structure is well designed for the two-stage catalytic removal of NO and NO2 in gases containing more than the 3% maximum oxygen level required for one stage removal. By applying platinum-alumina on the ceramic cartridge, excellent abatement (94%) of the nitrogen oxides present in the gases is achieved at 100 psi and space velocities up to 150,000.

13899

Varfamov, M. L., G. A. Manakin, Ya. I. Starosel'skiy, and L. S. Zhozhek

INVESTIGATION OF THE AMMONIA METHOD OF REMOVING NITROGEN OXIDES FROM THE EXHAUST GASES OF A NITROGEN-OXIDE NITRIC-ACID TOWER SYSTEM. I. (Issledovaniye ammiachnogo metoda ochistki ot okislov azota otkhodyashchikh gazov bashennoy nitroznoy sernokislotnoy sistemy). Text in Russian. Nauchn. Zap. Odessk. Politekhn. Inst., vol. 40:24-33, 1962. 4 refs.

Data from laboratory study of the removal of low concentrations of nitrogen oxides using gaseous ammonia and ammonia water are presented. The use of gaseous ammonia, in conjunction with acoustic coagulation with an aerosol, yielded an average degree of removal of 85% when incoming gases were highly oxidized. Nitrogen dioxide, and an equimolecular mixture of NO and NO2, reacted with 82-93% completeness with gaseous ammonia, this value increasing slightly with increased reaction volume. A gas lift using ammonia water yielded 63.6% purification with a 40% content of nitrogen oxides. The degree of oxidation of industrial exhaust gases is an important factor determining the degree of purification by this method. The data given correspond to an equimolecular NO and NO2 mixture.

14007

Hsieh, Yu Hsioh

AN EXPERIMENT IN THE PRODUCTION OF NITROGEN FROM NITRIC ACID PLANT TAIL GAS. (Ts'ung hsiao suan wei ch'i chih ch'i tʻan ch'i ti shih yen). Text in Chinese. K'o Hsueh T'ung Pao, vol. 10: 307-308, 1957. 6 refs.

By passing nitric acid tail gas first an alkali scrubbing tower to remove CO2 and then through a catalyst reactor to reduce NO2 and O2 in the presence of excess hydrogen, it was found practical to recover nitrogen. Three types of catalysts were made by depositing Cu and Ni on soil diatoms: CuO diatoms, NiO diatoms, and CuO plus NiO diatoms, all in a 1:9 ratio. The highest absorption rate could be attained with a sodium hydroxide concentration of 1% and a gas linear velocity of 0.2 m/sec. The concentration of CO2 could be reduced to 30 ppm. By using CuO with a firebrick carrier at a temperature of 600-650 C, a space velocity of 6000 reciprocal hours, and 4-6% excess hydrogen, it was possible to produce a gas with 1-5 ppm NO, 10-20 ppm 02, and 400 ppm NH3. By using the copper-nickel catalyst with diatoms as carriers at a temperature of 300-500 C, a space velocity of 1500 reciprocal hours, and 9% excess hydrogen, a gas with 0.4-0.7 ppm NO, 10-20 ppm 02, and 300-500 ppm NH3 could be produced with the content of noxious gas within acceptable limits. The temperature of reaction increases rapidly with oxygen content of the tail gas and with space velocity. Since the reactor was of simple construction, there was no way to control the temperature, and no tests were performed under conditions of low temperature and high space velocity.

14382

Pozin, M. E., B. A. Kopylev, and G. V. Bel'chenko

ABSORPTION OF NITROGEN OXIDES WITH A SODA SOLUTION IN A FOAM APPARATUS FOR THE PRODUCTION OF SODIUM NITRATE. (Poglosheheniye okislov azota sodovym rastvorom v pennom apparate dlya proizvodstva nitrata natriya). Text in Russian. Tr. Leningr. Tekhnol. Inst. Imen. Lensoveta, vol. 36:120-32, 1956. 12 refs.

A foam apparatus proved effective for the alkaline absorption of nitrogen oxides for the purpose of producing nitrates and decreasing the loss of nitrogen oxides in the production of nitric acid. The coefficient of efficiency of a single platform-cascade apparatus was decreased from 30 to 16% on increasing the linear gas flow rate from 0.5 to 3 m/sec in a cross section of the foam apparatus. The coefficient of absorption increases with increase in the linear flow rate of the gas, attaining a value of 1860 kg/sq m-hr-kg/cu m, which was approximately 6-7 times larger than the value of the absorption coefficient for a packed column under laboratory conditions, and 20-25 times greater than for factory-type scrubbers. With increase in the rate of flow of the liquid, the efficiency of a single platform of the apparatus and the coefficient of absorption increased insignificantly. Thus, increase in the rate of flow of the liquid by 3 times (from 1 to 3 cu m/hr) at a gas flow rate of 1 m/sec leads to an increase in efficiency of 22-24%. Increase in the concentration of absorbent in solution from 5 to 20% Na2CO3 at a linear gas flow rate of 1 m/sec leads to a decrease in efficiency from 26 to 16%. Correspondingly, the coefficient of absorption is also decreased. If the initial concentration of nitrogen oxides in the gas is increased from 0.05 to 1.4% at a linear gas flow rate of 1 m/sec, the value of the efficiency of a single platform of the apparatus increased from 8 to 25%. Choice of the number of platforms in the apparatus can be based on the data for a single platform in accordance with the required degree of absorption of nitrogen oxides.

14387

Nabiyev, M. K., A. A. Kulik, P. T. Merenkov, and A. D. Tikhonenko

PURIFICATION OF NITROGEN OF EXHAUST GAS IN THE PRODUCTION OF WEAK NITRIC ACID FOR THE SYNTHESIS OF AMMONIA. (Ochistka azota vykhlopnogo gaza pri proizvodstve slaboy azotnoy kisloty dlya sintera ammiaka). Text in Russian. Dokl. Akad. Nauk Uz. SSR, 20(11):17-20, 1963. 9 refs.

The small amount of nitrogen oxides in exhaust gases was reduced by natural gas using a nickel catalyst. On a platinum-nickel catalyst, a volume rate of 2800 cu cm was obtained. Complete purification occurred at 500-600 deg. The resulting gas containing 91.85% nitrogen, can be used for the synthesis of ammonia. A method is proposed for a single-step conversion to a nitrogen-hydrogen mixture using water vapor and nitrogen obtained by catalytic purification of exhaust gas.

14681

Van Der Drift, J.

CATALYTIC REMOVAL OF NITROGEN OXIDES FROM WASTE GASES OF NITRIC ACID PLANTS. A METHOD FOR THE PREVENTION OF AIR POLLUTION. (Katalytische verwijdering van N-oxyden uit afgewerkte gassen van salpeterzuurfabrieken. Een methode voor de bestrijding van luchtverontreiniging). Text in Dutch. Chem. Tech. (Amsterdam), 24(10):301-305, 1969. 11 refs.

Removal of nitrogen oxides from nitric acid plants can be achieved by catalytic decomposition or reduction. The cata-

lytic decomposition follows the reaction 2NO yields N2 plus O2. With a copper-silica gel catalyst, the nitrogen oxide content of waste gas was reduced from 892 to 277 ppm at 516 C. The reduction method uses hydrogen, natural gas, or ammonia as reducing agents. Various installations for the removal of nitrogen oxides from waste gases are described. A heat exchanger is used to lower the temperature of waste gases from around 515 C to 300 C after reduction. Several commercial catalysts are described. In an experiment using Honeycombgrid HCM-S-900 and ammonia, waste gas of 100,000 vol/vol catalyst/hr containing 0.3% nitrogen oxides and 3% O2 (inlet temp. 286 C) was reduced to 50 ppm NO2 and 86 ppm NO plus NO2. Using 0.3% Pt on a Torvex ceramic honeycomb and natural gas, waste gas of 100,000 vol/vol catalyst/hr containing 0.3% nitrogen oxides and 2.58% O2 (inlet temp. 440 C) was reduced to 58 ppm nitrogen oxides.

14533

A METHOD FOR THE RECOVERY OF NITROGEN OXIDES. (Werkwijze voor het winnen van stikstofoxyden). Text in Dutch. (Universal Oil Products Co., Des Plaines, Ill.) Dutch Pat. 6,607,036. 13p., Nov. 25, 1966. (Appl. May 23, 1966, 8 claims).

The system is particularly suited to handling tail gases from a nitric acid factory and from the lead chamber process of a sulfuric acid factory. This method also gives a distinct improvement in the output of a nitric acid plant. The waste gas is passed over a bed of adsorbing coal particles followed by a hot fluid desorption medium to remove the adsorbed nitrogen oxides from the particles. The desorption medium consists of steam at about 10 atm at a temperature greater than 157 C and preferably more than 177 C. The nitrogen oxide-containing steam is cooled and the mixture obtained is returned to the adsorption zone of the nitric acid plant. The desorption medium can also be hot air. The depth of the bed should not exceed 0.3m to prevent a large pressure drop. The stream waste gas through the adsorption bed is diverted upon saturation with nitrogen oxides to another bed of adsorbing coal. The coal in the first bed is then desorbed until the second bed is saturated and the cycle is repeated. Waste gas from sulfuric acid plants is treated the same way. The advantages of this method are better removal of nitrogen oxides with cost reduction, since no extra fuel is required. Due to integration of the units for preparation of acid and for recovery, higher output is obtained; output of a nitric acid plant can be increased by 5% by more complete use of NO2.

14568

Safiullin, N. Sh. and M. I. Olevinskiy

RENDERING HARMLESS THE WASTE GASES FROM SULFURIC ACID TOWER SYSTEMS. (Obezvrezhivaniye otkhodyashchikh gazov bashennykh sernokislotnykh sistem). Text in Russian. Khim. Prom. (Moscow), no. 3:132-136, 1955.

It is reported that a complex consisting of a precipitation section irrigated with strong acid and a moist electrofilter will assure reliable purification of waste gases from tower systems. Such a system reduces the aerosol and vapor sulfuric acid content to 0.04-0.10 g/cu m, a 20-fold reduction. Complete absorption of an equimolar mixture of nitrogen oxides results in a reduction in specific consumption rate of nitric acid by 6-8 kg/ton. Absorption of nitrogen oxides and reduction of nitric acid discharge rate may be increased significantly by supplying the equipment with nitrogen oxides with a degree of oxidation of 45-50%. In order to assure normal operation of the equipment, the amount of original sulfuric acid circulating in it must be not less than 80%. Joint operation of both the irrigating system and the electrofilter is imperative for proper purification of waste gases.

14664

Atsukawa, Masumi, Yoshihiko Nishimoto, and Naoyuki Takahashi

STUDY ON THE REMOVAL OF NITROGEN OXIDES FROM EFFLUENT STACK GASES. Mitsubishi Heavy Industries, Ltd., Tech. Rev., 5(2):129-135, May 1968. 9 refs.

Pilot plant tests of the Mitsubishi process for removing nitrogen oxides from stack gases demonstrate that nitrogen oxides can be economically reduced to less than 0.02% of gas content. By limiting threshold concentrations of nitric acid to 200 ppm or below, the method should meet the removal requirements of the major sources of nitrogen oxide emissions: metal pickling plants, nitric acid plants, chemical plants using nitric acid, nitrate, and nitrite plants. Nitric oxide is converted to NO2 by either homogeneous or catalytic oxidation, while nitrogen compounds are recovered through absorption of stack gases in wetted-wall towers packed with PVC sheets. Homogeneous oxidation is a slow process and requires large equipment. However, this equipment is easy to operate. Catalytic oxidation can be performed on small-scale equipment, but the catalyst is affected by water, dust, and mist present in the effluent gas and regeneration is necessary. The PVC equipment has a large absorption coefficient and a small pressure drop.

15152

Schwanecke, Rudolf

WASTE GAS CLEANING THROUGH COMBUSTION OF NITROGEN OXIDES. (Abgasreinigung durch Verbrennen von Stickstoffoxyden). Text in German. Zentr. Arbeitsmed. Arbeitsschutz, 19(9):262-264, 1969. 3 refs.

Various methods for elimination of NO and NO2 from waste gases are reviewed. Absorption of the nitrogen oxides on silica gel has recently interested the nitric acid plants. Water vapor is used for desorption, and the recovered nitrogen oxides are returned to the nitric acid plant. If no recovery of the nitrogen oxides is desired, they can be removed from waste air by scrubbing with water or bases such as sodium hydroxide or ammonia water. The reaction follows the equation 3NO2 + H2O yields 2HNO3 + NO. As can be seen, only NO2 is removed. A patented process for dissociation of NO and NO2 in the reducing part of the flame is based on the reaction of carbon monoxide with NO2 and NO in a flame sustained in an atmosphere of low air. The reaction follows the equation 2NO + 2CO yields N2 + 2CO2. It has also been discovered that the nitrogen oxides dissociate in an atmosphere of 20% or more excess air. The process depends on the thorough mixing of the gases with the flame, as accomplished by atomization. In a chemical plant, NO and NO2 are eliminated by a combination of scrubbing and combustion. Nitric oxide escapes from the scrubber at a rate of up to 30 cu m/hr with a temperature of 30 C. It is mixed with air and atomized with the fuel oil in a muffle furnace; it serves as combustion air and as an atomizing agent for the fuel oil. About 3 to 5 ppm of NO and NO2 were measured in the waste gas of the furnace.

16726

Kazakova, E. A., R. Z. Khiterer, and V. E. Bomshtein

PURIFICATION OF EXHAUST GASES FROM NITRIC ACID PLANTS. Brit. Chem. Eng., 14(5):667-668, May 1969.

The presence of unabsorbed nitrous gases in the tail gases from nitric acid plants created a serious pollution problem and

efforts to deal with it have followed various lines. In this article a pilot plant that applies the principle of adsorption of the nitrogen oxides by a fluidized stream of silica gel particles is described. The pilot plant consisted of an adsorption column operating at 5.5 atm and a desorber operating at atmospheric pressure. In the adsorption column, fluidized silica gel flows counter-current to the gas stream. The NO is partly oxidized to NO2 and adsorbed on the silica gel. The adsorbent saturated with NO2 is withdrawn from the adsorber base and passes to the desorption column. Here the adsorbent is heated with steam to 180 to 190 C while a current of air desorbs the silica gel. The desorption products, after dedusting in a cyclone are returned to the process.

19847

Karakova, E. A., R. Z. Khiterer, and V. E. Bomshtein

PURIFICATION OF EXHAUST GASES FROM NITRIC ACID PLANTS. Brit. Chem. Eng., 14(5):667-668, May 1969. (Also: Khim. Prom. (Moscow), vol. 7:517, 1968.)

A method for adsorbing the exhaust gases from a nitric acid plant is discussed. Exhaust gases were cooled with water and brine to 0 C, and after separation of condensate, entered the 500 mm diameter adsorption column. This has 22 trays spaced at 400 mm, and fluidized silica gel flows from tray to tray, countercurrent to the gas stream. Nitric oxide is partly oxidized to nitrogen dioxide and is adsorbed on the silica gel. The adsorbent saturated with NO2, is withdrawn from the adsorber and passed to the desorption column. This column is heated with steam to 180 to 190 C, while an air current desorbs the silica gel. The desorption products, containing 65% acid vapor, water, NO2, nitrogen, and oxygen, after dedusting in a cyclone, are returned to the process. It was found convenient to locate the adsorption column above the desorber, and to conduct both operations at 5 atm. A gate valve controls the flow between columns; a pneumatic conveyer transfers the adsorbent from column base to column head. By raising the temperature in the desorber to 190 C, the nitrogen oxides concentration can be reduced to 0.01%.

20313

Newman, Daniel J. and Jorge M. Matta

APPARATUS FOR NITROGEN OXIDES ABSORPTION TO PRODUCE CONCENTRATED NITRIC ACID. (Chemical Construction Corp., New York, N. Y.) U. S. Pat 3,499,734. 7p., March 10, 1970. 4 refs. (Appl. Jun. 5, 1967, 14 claims).

An apparatus is provided for the absorption of nitrogen oxides from a gas stream into an aqueous absorbent solution to form nitric acid, in which re-oxidation of nitric oxide also takes place. The apparatus is provided with a lower combination heat exchanger-absorber section in which the simultaneous absorption of nitrogen dioxide, re-oxidation of nitric oxide, and cooling of the liquid phase takes place. Two or more heat exchanger sections may be provided in series. A gas-liquid contact section such as a packed section or a plurality of perforated trays is provided above the heat exchanger sections. The feed gas stream containing nitrogen oxides and excess free oxygen is passed into the apparatus below the heat exchanger sections, while the aqueous absorbent solution is admitted above the upper gas-liquid contact section. (Author abstract)

20775

Ermenc, E. D.

CONTROLLING NITRIC OXIDE EMISSION. Chem. Eng., 77(12):193-196, June 1, 1970. 1 ref.

Industries using nitric acid in their processes should now be planning to meet the anticipated legal standards, which may limit emissions of nitrogen oxides to about 500 ppm. Data for controlling emissions are presented. The reaction kinetics of nitrogen and oxygen in air are characterized at high temperatures by standard second-order equations, while the reaction becomes zero orders at temperatures below 2025 F. Because the reverse reaction rate is many times greater than the forward rate, cooling must be very rapid to retain nitric oxide, and very slow to promote its reversion to oxygen and nitrogen. The problem of pollution control is that most processes involving high temperatures are designed for minimum residence time (i.e., rapid cooling) to reduce capital requirements. Below 3200 F, the rate of formation controls nitric oxide production; above 3200 F, the reverse rate is the controlling factor. Nitric oxide production departs from equilibrium at a maximum around 2800 F, and then approaches equilibrium at 3200 F. As 3200 F is passed, the departure from equilibrium becomes more pronounced with rising temperature, showing the effect of the reverse reaction rate. Emissions could be lowered by some of the following means: better recovery through refrigeration, cooler circulating acid, or the compression of nitrogen oxides after the condensing phase; a good balance of oxygen after condensation to oxidize nitric oxide; catalytic incineration of tail gases to reduce nitrogen oxides to nitrogen and oxygen; and further absorption tail gases in an alkaline tower followed by catalytic incineration. Besides being a function of temperature, the formation of nitric oxide also depends on the amount of excess air used in a process.

21232

Hunter, J. B.

PLATINUM CATALYSTS FOR THE CONTROL OF AIR POLLUTION. A TAIL GAS REDUCTION SYSTEM FOR NITRIC ACID PLANTS. Platinum Metals Rev., vol. 9-12:2-6, 1965-1968. 1 ref.

Effective reduction of nitrogen oxides, hydrocarbons, and organic vapor is obtained by the use of platinum catalysts supported by a ceramic honeycomb. Use of the ceramic honeycomb support overcomes the two principle objections to platinum as a catalyst in pelletized form, pressure drops across pelleted beds, and loss of fines. Other important advantages for honeycomb catalysts are the elimination of hot spots, more uniform gas distribution, greater structural strength, and no channelling. From the standpoint of system design, the rigid structure also provides greater process flexibility. Horizontal as well as vertical reactors may be used. In nuclear power installations, intense radiation causes the decomposition of water into a hydrogen/oxygen mixture. Platinum honeycomb catalysts are effective as hydrogen/oxygen recombiners.

23172

Teske, W.

EMISSIONS AND ABATEMENT OF OXIDES OF NITROGEN IN NITRIC ACID MANUFACTURE. Chem. Engr. (London), 46(7):263-266, Sept. 1968.

The 12 nitric acid factories in West Germany, producing acid mainly for use in fertilizers, emit a total of about 100 tons/day of nitric oxide. Stack gases have a brown color, due to a visibility limit of 200 ppm NO. New plant construction is of the pressure type, in which the NO content of the stack gases is about half that of older plants. The NO content of these gases is due to the incomplete conversion, or the absorption yield, of NO to nitric acid. Thus, to eliminate the NO in the waste gases, the absorption yield must be increased or the NO destroyed. Various absorption processes are briefly reviewed

in terms of possibilities for accelerating absorption, but total absorption in an acid system is not practical. Catalytic reductant processes reduce nitrogen oxides by means of hydrogen, hydrocarbon gases, or ammonia, and can be carried out in two stages: partial reduction of the NO2 to NO (decoloring the waste gases), and total reduction of NO and NO2 to N2. Because the price of the reducing agent is a decisive factor, an attempt should be made to decompose the nitrogen oxides directly, which would permit general adoption of catalytic purification by the nitric acid industry.

25880

Stankus, L.

NAPCA'S SEARCH FOR FLUE GAS DESULFURIZING PROCESSES. Preprint, 22p., 1969 (7). (Presented at the Gordon Research Conference, Aug. 18-22, 1969.)

The National Air Pollution Control Administration's work on sulfur oxides and nitrogen oxides control is summarized by briefly stating the scope of major investigations, showing principal concepts generated, and indicating present achievements and possible future developments. There are several methods for desulfurizing flue gases under investigation, such as ammonia scrubbing and aqueous scrubbing. Organic liquids, such as olefins, carbohydrates, and amines, appear promising for extracting sulfur dioxide from flue gas. Solid organic materials including newsprint, sawdust, and cotton are capable of absorbing SO2. The most suitable catalyst for oxidizing SO2 to SO3 is vanadium pentoxide. Several methods for reducing SO2 to elemental sulfur were also investigated. Coal gasification was studied as a method for eliminating the various forms of sulfur contained in coal. Methods for reducing nitrogen oxides emissions include catalytic reduction, staged combustion, and fuel combustion with oxygen. Combustion with low excess air, steam or water injection into the fuel burning zone, and flue gas recirculation into the fuel-air mixture were also investigated. A study on the availability and use of natural gas as a sulfur-free fuel for power generation was conducted. The principal chemical reactions that occur with these control methods are included.

25714

Fuchs, Andrew B. and James C. Moore

CHEMICAL SUPPRESSION OF NITROGEN OXIDES. (Grace (W. R.) and Co., New York) U. S. Pat. 3,528,797. 5p., Sept. 15, 1970. 2 refs. (Appl. Nov. 8, 1967, 6 claims).

A scrubbing apparatus containing urea is provided which substantially eliminates all nitrogen oxides that are formed as by-products of the phosphate fertilizer manufacturing process. Urea when dissolved in water reacts with nitrogen oxide and nitrogen dioxide gases to produce nitrogen, carbon dioxide, and water. The preferable range of urea is 0.1 to 0.3 weight percent, based on the total weight of the batch size, and it may be employed in an aqueous scrubbing tower or added to the acidulation mass.

26071

AIR POLLUTION. Chem. Process., 16(11):11, 13, Dec. 1970. 7 refs.

Nitric acid manufacture, nitrogen processes, and dissolving operations using nitric acid contribute the major portion of oxides of nitrogen emitted to the atmosphere by non-combustion processing. Several methods which exist for the control of these oxides from stack gases include catalysis, adsorption, absorption, and direct flame incineration. Palladium on a particulate alumina support and a ceramic catalyst are recommended for nitric acid tail gas purification. Adsorption on molecular sieves appears economically attractive where high oxygen concentrations preclude non-selective catalysis. Absorption in liquids, while technically feasible, usually introduces by-product disposal problems. Direct flame incineration is most effective for reduction of nitrogen dioxide to nitric oxide. Modifications for combustion processes include low excess air, staged combustion, flue gas recirculation, steam and water injection, combustion with oxygen, and fluidized bed combustion.

C. MEASUREMENT METHODS

02570

M.D. Manita V.P. Melekhina

A SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF NITRIC AND HYDROCHLORIC ACIDS IN THE ATMOSPHERIC AIR IN THE PRESENCE OF NITRATES AND CHLORIDES. (Spektrofotometricheskii metod opredeleniya azotnoi i solyanoi kislot v prisutstvii nitratov v atmosfernom voz'dukhe.) Hyg. Sanit. 29, (3) 62-6, Mar. 1964. CFSTI: TT65-50023/3

A spectrophotometric method for the determination of hydrochloric and nitric acids in the presence of nitrates and chlorides is described. This method is based on the determination of the optical density of colored aqueous solutions containing the above acids after the addition of methyl red in ethanol. The sensitivity of the method is 0.18 microgram of HCl. per ml and 0.31 microgram of HNO3 per ml. Other acids and bases interfere with the assay. CO2 and SO2 always present in atmospheric air do not interfere with the spectrophotometric determination of hydrochloric and nitric acids when this is carried out under the conditions described.

04257

E. Kh. Gol'dberg

PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF VOLATILE MINERAL ACIDS (HYDROCHLORIC AND NITRIC) IN THE ATMOSPHERE. (Fotometricheskoe opredelenie malykh kolichestv letuchikh mineral'nykh kislot (solyanoi i azotnoi) v atmosfernom vozdukhe.) Hyg. Sanit. 31, (9) 440-3, Aug. 1966. Russ. (Tr.) CFSTI: TT 66-51160/7-9

A spectrophotometric method was recommended for the analysis of low concentrations of mineral acids in the atmosphere. However, it is not always possible to use this method at the laboratories of the district sanitary-epidemiological centers because of the absence of a spectrophotometer. Modification of the spectrophotometric method for purposes of photometric determinations with a photoelectrocolorimeter required a calibration graph for the relationship between the optical density and the concentration of hydrogen ions in micrograms per 1 ml for an FEK-56 photoelectrocolorimeter. Standard solutions were prepared from fresh 0.005 N HCl and HNO3. Solutions were made containing 0.005 to 0.02 microgram/ml H+. A zero solution (distilled water) was prepared simultaneously. In all cases, an addition was made of 0.4 ml 0.01% alcohol solution of methyl red. The optical density of standard solutions and of a zero solution with the methyl red reagent was determined with respect to distilled water. This photometric technique made possible the establishment of constant optical densities of aqueous solutions of acids in the standard scale, independent of the pH of the distilled water used. The sensitivity of the photoelectro colorimetric method and the sampling procedure are the same as for the spectrophotometric method. Studies were also made of the possibilities of visual colorimetric determinations. It was found that in the absence of a photoelectrocolorimeter the solutions can be determined colorimetrically by visual means by the method of standard series with an artificial scale.

06809

Antoshechkin, A. G.

INSTRUMENT FOR DETERMINATIONS OF THE CONCENTRATIONS OF NITROGEN OXIDES AND NITRIC ACID FUMES IN AIR. (Pribor dlya opredeleniya kontsentratsii okislov azota i parov azotnoi kisloty v vozdukhe.) Hyg. Sanit. (Gigiena i Sanit.), 30(2):234-236, Feb. 1965. Translated from Russian. CFSTI: TT 65-51033

The author designed and tested an instrument for the determination of the concentrations of nitrogen oxides and nitric acid fumes in air. The action of the instrument is based on measurements of the electrical conductivity of a solution obtained by drawing the air with nitrogen oxides through distilled water. The instrument is portable, its design is simple and it can be constructed under laboratory conditions. Its sensitivity is from 0.003 to 20 mg nitrogen oxides per 1 liter of air. One analysis takes 1 to 2 min. Thirty ml of distilled water is introduced with the syringe into the upper tube and into the vessel. The water cannot leave the vessel because of the valve, and it forms a 1 cm layer between the two electrodes. now the pump is attached and 5 l of air are drawn in distilled water. Nitrogen oxide from the air combines with water to produce nitrous acid. The higher the concentration of nitrogen oxide in the air, the higher will be the concentration of the HNO2 solution in the vessel. Since HNO2, like HNO3, is a strong electrolyte and completely dissociated to ions in dilute solutions, the electrical conductivity of the solution is proportional to the concentration. The electrodes are fed with a constant voltage from a 4.5V source. In using the instrument, one must remember that interference is caused by gases that are readily soluble in water and produce a strong electrolyte on solution (the sulfuric acid fumes). After suitable graduation, the instrument can also be used for the determination of sulfuric acid fumes in air.

111301

Saltzman, Bernard E.

METHODS OF MEASURING AND MONITORING ATMOSPHERIC NITROGEN OXIDES AND THEIR PRODUCTS. (Part I.) World Health Organization, Geneva, (Switzerland). WHO/AP/68.31,99p., 1968. (93) refs.

A working text of NOx measurement methods in common use is presented. Sufficient details are provided so that no additional material should be needed to conduct the analysis. However, abundant references are provided. The actual texts of methods which have been selected by appropriate organizations are quoted in exact form. Measuring and monitoring atmospheric nitrogen oxides are complex because of the fact that many interrelated oxides and products exist. These undergo chemical reactions and equilibria both in the atmosphere and in air sampling apparatus. The effects of the various substances are different. Their interferences also differ for various analytical procedures. Therefore to fully expose the provisos in making these measurements, an introductory section is presented giving chemical and physical properties, various reaction rates, and equilibrium data. In these analyses we

are seeking to measure concentrations that vary both in time and space. Rational design of a sampling program therefore requires a knowledg of these distribution patterns. Only then can we clarify the effects of sampling time, numbers of sampling locations, numbers of samples collected, and correlate these with the objectives which ar sought. These topics therefore also are included.

18226

INVESTIGATION AND APPRAISAL OF FLU-GAS DAMAGE. (Untersuchung und Begutachtung von Rauchschaden. Part I.). Translated from German. Hamburg Staatsinstitut fur Angewandte Botanik Jahresbericht, 5(119-120), 1938. 3 refs.

Plants exposed to flue gas showed definite damage from fluorine (F) and acids of sulfur and nitrogen. A crystalization method utilizing the microscopic identification of silico-sodium fluoride proved best for qualitative fluorine analysis of the 102 samples examined through 1936. As in previous studies, the samples tested showed that F was taken in through the branch bark and leaves of cherries and pears. For the first time, however, the fruit itself was damaged and F detected there. Black, hard disks had formed around the flower and in the fruit adjacent to the flower. Samples examined long after damage took place showed no F present. Twenty-one samples were examined for acid damage. Large concentrations of nitrates were detected in the specimens by means of the diphenylamine-sulfuric acid reaction. Different plant species showed markedly different sensitivities to flue gases.

23560

Aleksandrov, Yu. I., V. D. Mikina, and G. A. Novikov

CORRECTION FOR OXIDATION OF NITROGEN IN THE DETERMINATION OF HEAT OF COMBUSTION. Tr. Vses. Nauch.-Issled. Inst. Metrol., 111(171):95-102, 1969. 11 refs. Translated from Russian by D. P. Biddiscombe, Ministry of Technology (England), Div. of Chemical Standardds, 11p., March 1970. CFSTI: N70-28918

At present, the heat effect due to oxidation of nitrogen in a calorimetric bomb is computed on the basis of determination of the amount of nitric acid after the calorimetric experiment by titration of the bomb liquid with a 0.1-N solution of alkali; methyl orange is used as indicator. Results obtained during a prolonged period of work, by titration of bomb liquid after combustion of benzoic acid, differed one from another more than was to be expected from the errors of the titration method. Analysis of literature data on the formation of nitric acid does not give a thorough explanation of this discrepancy in titration results. To elucidate the reasons for this discrepancy, a study was made of the dependence of the amount of nitric acid formed upon the ageing time of the combustion products in the bomb, upon the initial concentration of nitrogen, upon the size of the flame, and upon the pressure of oxygen in the bomb. Study of the process of oxidation of nitrogen in the calorimetric bomb has established that, by the end of an experiment, when the bomb is opened, the reaction between nitrogen dioxide and water is not complete, and thus the end-product contains not only nitric acid, but also nitrogen dioxide. By the end of the main period, the amount of each component depends upon the initial concentration of nitrogen in the oxygen, the size of the flame during combustion of the substance, and the time of flushing of the bomb with oxygen. The amount of nitric acid formed depends upon the time of ageing of the combustion products in the bomb. In calorimetric practice at the present time, only the process of nitric acid formation is taken into account. On the basis of the investigations carried out, a procedure for determining the correction for oxidation of nitrogen, taking account of the incomplete conversion of oxides of nitrogen into nitric acid, is advised. In order to determine more precisely the make-up of the correction, the methods of its determination must be changed. To calculate the correction, it is necessary to determine the amount of nitric acid formed by the end of the main period of a calorimetric experiment and thus establish the amount of nitrogen dioxide present at that time in the gas phase in the bomb.

23771

Patton, W. F. and J. A. Brink, Jr.

NEW EQUIPMENT AND TECHNIQUES FOR SAMPLING CHEMICAL PROCESS GASES. J. Air Pollution Control Assoc., 13(4):162-166, April 1963. 7 refs (Presented at the Air Pollution Control Association, 55th Annual Meeting, Chicago, May 20-24, 1962.)

When the need for improved sampling equipment and techniques was recognized at Monsanto a number of years ago, a cascade impactor suitable for adiabatic measurements on process gases was developed. Simpler equipment, suitable for routine control of air pollution, can determine accurately the weight or chemical composition of the particles in a gas stream, as well as separately determine the loading of particles greater thru three micron in diameter from particles smaller than this. The dust or mist sampling device is contained in a small case with a carrying handle and removable sides similar to an Orsat analyzer. Gases first enter the cyclone where the larger particles are collected, while the smaller particles are carried over and collected by the filter. Sampling preparations are discussed for large particles, fine particles, and isokinetic sampling. The procedures for sampling are outlined, as well as an example for sulfuric acid mist. Calculations of loadings from sampling data are also indicated. Eight sets of the sampling equipment have been utilized for sulfuric, phosphoric, and nitric acid mists, mercury mist, various phosphate salt dust, ammonium chloride fume, ammonium nitrate fume, and several organic mists.

24725

Lesoine, L. Grant

EFFECT OF PARTICLE SIZE ON THE DETERMINATION OF INORGANIC SULFUR IN COAL. In: Report of Bituminous Research Activities. Pennsylvan State Univ., University Park, Dept. of Fuel Technology, Serial No. 57, p. 1-8, 1956. 8 refs.

The effect of reducing the standard 60-mesh coal samples to micron size was investigated to determine if the size of the coal materially quantitatively affects the determination of inorganic sulfur using the Eschka, and Powell and Parr Methods. A significantly higher inorganic sulfur content was obtained with micron-size coal. The pyritic iron content also increased in the same proportion. This leads to the conclusion that finely divided pyrite is intimately associated with the coal substance and is made more amenable to reaction with nitric acid when ground to micron size. Since both the sulfur and iron contents increased proportionally, it appears doubtful that any sulfur-bearing inorganic material other than pyrite is present in any significant quantity in the occluded matter. The iron content calculated to percent sulfur was greater in all cases than the actual total inorganic sulfur. Hence, it is assumed that acid extraction of the coal did not remove organic sulfur from these coals. The difference in values leaves a question as to the dependability of the usual inorganic sulfur analysis or to the validity of the term 'inorganic' sulfur as applied to acid-extractable sulfur. (Author summary modified)

24975

Grigorescu, I. and L. Bengeanu

SPECTROCOLORIMETRIC DETERMINATION OF HEXACHLOROCYCLOHEXANE IN THE ATMOSPHERE. (Dozarea hexaclorciclohexanului in atmosfera prin metoda spectrocolorimetrica). Text in Rumanian. Rev. Chim. (Bucharest), 18(9):565-566, 1967. 7 refs.

This broad-spectrum insecticide is finding an increasing use, so that accurate detection measures are necessary for its proper control. A method has been adopted by the Central Toxicology Laboratory of the Rumanian Ministry of Chemical Industries, which makes use of chloride-free toluene, sodium hydroxide dissolved in 0.1 N ethyl alcohol, a 1% solution of ferric ammonium sulfate in 15% nitric acid, a 0.1% solution of mercuric sulfocyanide in 96% ethyl alcohol, and a standard solution of HCH prepared by dissolving 0.5 g of lindane in 100 cc of toluene, from which a working standard is prepared by dilution, which contains 500 micrograms per cubic centimeter of HCH. Air samples are collected with an impinger containing 100 cc of toluene, through which the air is caused to flow at the rate of 10-15 cu m /minute, the total volume of the sample being dependent on the suspected amount of atmospheric HCH, on the average about 10 cu m. Given the extent of the sample-collecting time, the presence of chlorine and inorganic chlorides in the atmosphere will not create interference with the determinations, but special care must be taken to eliminate all chloride impurities from the reagents used. Testing of the method indicates that the margin of error can amount to plus or minus 10%, with an average error of 3%. The amount of time required for determination is 20 minutes, on the average.

25381

(Inventor not given.)

DETECTION OF MISSILE FUELS IN GAS ATMOSPHERES. (Mine Safety Appliances Co., Inc., Pittsburgh, Pa.) Brit. Pat. 1,151,954. 3p., May 7, 1969. 5 refs. (Appl. May 26, 1966, 16 claims)

A simple, rapid, and reliable method is described of detecting the presence in a gas of a volatile nitrogen compound of the group consisting of hydrazine, hydrazine hydrate, red fuming nitric acid, nitrogen dioxide, unsymmetrical dimethyl hydrazine, and alkyl hydrazines. A variety of volatile nitrogen compounds are used as components of missile fuels, and various hazards are attendant upon the fueling, handling and storing of missiles propelled by such liquids. In the presence of the above mentioned nitrogen compounds, and also nitrogen dioxide, a particularly effective color change is produced when a hexavalent chromium compound and the pentavalent phosphoric acid are present in proportions providing from 0.0145 to 2.6 grams of hexavalent chromium and from 0.022 to 24 grams of pentavalent phosphorus, per 100 ml of carrier.

25925

Cauer, H.

SOME PROBLEMS OF ATMOSPHERIC CHEMISTRY. In: Compendium of Meteorology. T. F. Malone (ed.). Boston, American Meteorological Society, 1951, p. 1126-1136. 60 refs.

Satisfactory methods for the chemical analysis of air will evolve only when analytical chemists are also adequately trained in physical chemistry and physical meteorology. A second requirement is further development of methodology. Not until the development is more or less complete will it be possible to undertake a third major task, that of making many parallel investigations in micrometeorological as well as worldwide networks under the most varied atmospheric conditions and at various heights above the ground. Of the chemical methods available today, [illegible] methods developed in Europe are briefly discussed: the absorption-tube method for detecting the presence of secondary gaseous substances, and the condensation method for the analysis of water-soluble atmospheric constituents which form condensation nuclei. Results obtained by both methods are evaluated and suggestions are made for further research. To explain condensation (cloud formation), the chemist must have recourse to intermolecular forces and, in the last analysis, to processes of atomic energy. Four types of short-range molecular forces are discussed in light of existing knowledge. It is anticipated that the first chemical techniques developed for the field of dynamic meteorology may be connected with determinations of the pH value and the reduction power of aerosols. Such uses would provide accurate information about the motion of air masses and the degree of turbulence.

E. ATMOSPHERIC INTERACTION

14408

Rhine, P. E., L. D. Tubbs, and Dudley Williams

NITRIC ACID VAPOR ABOVE 19 KM IN THE EARTH'S ATMOSPHERE. Appl. Opt., 8(7):1500-1501, July 1969. 6 refs.

Atmospheric data obtained from balloon flights by other investigators suggested that previously unreported atmospheric bands at approximately 30 km and a solar zenith angle of 90 deg were caused by the association of nitric acid vapor with the ozone layer. To estimate the amount of nitric acid vapor in the atmosphere at this altitude, atmospheric nitric acid vapor was experimentally measured in an absorption cell in the spectral regions of 1240-1380 inverse cm and 810-940 inverse cm. Laboratory and atmospheric data were compared by integrated spectral absorbance. Approximately 10% of the total absorbance in both laboratory and atmospheric spectra is associated with Q branches at the overlapping bands 879 and 897 inverse cm, and it is concluded that any observable nitric acid vapor contributions to solar absorption spectra at low altitudes would be connected with these band Q branches. Production of nitric acid vapor in the ozone layer may proceed according to the reactions H plus O3 yields O2 plus OH*, or OH plus NO2 yields HNO3. The second reaction is presumed to be enhanced by darkness.

21534

Leighton, Philip A.

REACTIONS AND EQUILIBRIA OF THE OXIDES AND OXY ACIDS OF NITROGEN. *In:* Photochemistry of Air Pollution. New York, Academic Press, 1961, Chapt. 7, p. 184-200.

Certain reactions involving the oxides and oxy acids of nitrogen occur simultaneously with the photochemical reactions of these products. Both the equilibrium and the rate of reaction of nitric oxide with molecular oxygen have been established over a broad temperature range. Reactions involving nitrogen trioxide which are necessary to explain the major behavior of the oxides of nitrogen are given. The reaction of nitric oxide and nitrogen dioxide with water to give nitrous acid has been quantitatively studied. Nitrogen dioxide reacts slowly with unsaturated hydrocarbons, even in the dark. Pure nitric acid can be stored in contact with liquid olefins for days without reaction, but if a trace of nitrogen dioxide is present, reaction occurs. There is no evidence that the reactions of oxides and oxy acids with aldehydes, organic acids, and other organic compounds are fast enough to be of any importance. Rates and equations for the various reactions are discussed.

21642

Leighton, Philip A.

ABSORPTION RATES AND PRIMARY PHOTOCHEMICAL PROCESSES. In: Photochemistry of Air Pollution. New York, Academic Press, 1961, Chapt. 3, p. 42-99.

For any photochemical reaction, the primary chemical process is the first chemical step following the act of absorption of radiation. In the lower atmosphere, the absorbers will be the species which absorb in the photochemically active region of the solar spectrum. Ordinary oxygen absorbs very faintly in the red end of the visible spectrum. Gaseous ozone absorbs strongly in the region 2000-3500 A. Nitrogen dioxide absorbs over virtually the entire visible and ultraviolet range of the solar spectrum in the lower atmosphere. Gaseous sulfur dioxide shows absorption consisting of bands with sharp rotational structure. Nitric acid and the organic nitrates show continuous absorption which extends to some extent into the solar ultraviolet. Compounds containing a carbonyl group all show absorption in the solar radiation range. Acyl and peroxyacyl nitrates and nitrites are discussed at length. Reactions following absorption by particulate matter are discussed. Rates and equations of the various reactions are included.

22407

Vohra, K. G. and P. V. N. Nair

RECENT THINKING ON THE CHEMICAL FORMATION OF AEROSOLS IN THE AIR BY GAS PHASE REACTIONS. Aerosol Sci., vol. 1:127-133, 1970. 11 ref.

Possible mechanisms of formation of aerosols in the air by chemical reactions in the gas phase are described. In the basic reactions, formation of hydrochloric acid, sulfuric acid, and nitric acid molecules from chlorine, sulfur dioxide and oxides of nitrogen, in the presence of water vapor, are considered along with the role of solar radiations, ionizing radiations, electric discharges and ozone in the formation of these acids. Formation of nuclei by the hydration of acid molecules and their reaction with other organic and inorganic trace gases are also discussed. The reactions important in the formation of Aitken nuclei and aerosols are mainly oxidation, hydration, acid-base reactions and addition and recombination reactions. In these reactions, the combined role of solar and ionizing radiations are considered. The formation of embryos and growth of particles in the humid air are discussed on the basis of Raoult's law. The important role of chemically formed particles in the atmospheric processes and the possible impact of nuclear power production on the nuclei content of the atmosphere are suggested. (Author abstract modified)

23037

Altshuller, Aubrey P.

THERMODYNAMIC CONSIDERATIONS IN THE INTERACTIONS OF NITROGEN OXIDES AND OXY-ACIDS IN THE ATMOSPHERE. J. Air Pollution Control Assoc. 6(2):97-100, 1956. 15 refs. (Presented at the Air Pollution Control Association, 49th Annual Meeting, Buffalo, N. Y., May 20-24, 1956.)

Equilibrium constants, calculated from recent spectroscopic and structural measurements, are reported for some nitrogen dioxide reactions. From these constants, estimated concentrations of gaseous nitrogen oxides and oxy-acids in urban atmospheres were calculated. It is emphasized that the equilibrium conditions to which the data apply may be reached very slowly or rapidly, or at some intermediate rate. Determination of this rate is a problem for experimental kinetics rather than thermodynamics. The value of thermodynamic information is that it can tell whether a small or large amount of a given reactant will exist at equilibrium. The present thermodynamic

study indicates that among the nitrogen oxides and oxy-acids, nitric oxide, nitrogen dioxide, and nitric acid are probably the most prevalent in polluted urban air. Nitrous oxide is also present in urban air but is of less importance because of its lower chemical reactivity.

23604

Nicolet, M.

THE ORIGIN OF NITRIC OXIDE IN THE TERRESTRIAL ATMOSPHERE. Planetary Space Sci., 18(7):1111-1118, July 1970. 32 refs.

Recent observations in the stratosphere, mesosphere, and thermosphere indicate that nitric oxide is present in significant amounts, even though its local production seems to be very small. Reactions which might account for an indirect way of production are discussed. Nitric oxide in the stratosphere and mesosphere may be due to downward transport from the thermosphere. Photochemical reactions, including photodissociation, are described. Balances of reactions of formation and removal of nitric oxide and atomic nitrogen are considered. In the lower thermosphere, the downward current of NO molecules depends on the value of the eddy diffusion coefficient. In the stratosphere, the final sink of NO and NO2 is the formation of HNO2 and HNO3 by reactions with HO2 and H2O2. A small eddy diffusion coefficient is required.

24015

Altshuller, Aubrey P.

THERMODYNAMIC CONSIDERATIONS IN THE INTERACTIONS OF NITROGEN OXIDES AND OXY-ACIDS IN THE ATMOSPHERE. Preprint, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, 16p., 1956 (?). 16 refs.

The thermodynamic equilibrium constants are computed for a number of chemical reactions involving nitrogen oxides and oxy-acids. The nitrogen oxides likely to be present in any substantial quantity in the atmosphere are nitrous oxide, nitric oxide, and nitrogen dioxide. The concentrations of reactants and products in these reactions at chemical equilibrium are given, and the rates at which these reactions proceed towards equilibrium are discussed. Most of the reactions considered are 'dark' reactions, but the importance of photochemical reactions involving ozone is pointed out and the photolysis of nitrogen dioxide is discussed in detail. The varying importance of the individual reactions of nitrogen oxides in air pollution problems is emphasized. (Author abstract modified)

F. BASIC SCIENCE AND TECHNOLOGY

01619

NITRIC ACID MANUFACTURE (INFORMATIVE REPT. NO. 8). J. Air Pollution Control Assoc. 14, (3) 91-3, Mar. 1964. (TI 2 Chemical Industry Committee).

Nitric acid manufacture by the ammonia oxidation process and the concentration process are described. The control aspects are discussed.

10160

Gaaz, S. N.

EFFECT OF HYDRODYNAMIC CONDITIONS ON RATE OF NITROGEN OXIDES AB- SORPTION BY Ca(OH)2 SOLUTION, WITH THE AID OF A MECHANICAL AB- SORBER UNDER SEMI-INDUSTRIAL CONDITIONS. (COMMUNICATION I.) Zh. Prikl. Khim., 30(9):1311-1320, 1957. 5 refs. **Translated from Russian by B. S. Levine, U. S. S. R. Literature on Air Pollution and Related Occupational Diseases, Vol. 6, 299 p., April 1961. CFSTI: TT 61-21982**

The effect of hydrodynamic conditions on the rate of nitrogen oxides absorption by a solution of Ca(OH)2 was studied with the aid of a rapidly rotating mechanical absorber under semi-industrial conditions, using industrial gas from a nitric acid shop. The in vestigations were conducted in 2 stages: 1) a study of the effects of the system's hydrodynamic, physical and chemical factors on the absorption rate; during this study the installation was operating periodically for time intervals determined by the requirements of each test; the phases investigated were: the effect of the peri pheral speed of discs, the volume rate of gas flow, the quantity of liquid in the absorber, the CaO and nitrite-nitrate salt concen- trations in the solution, the degree of gas oxidation, etc.; 2) during the second stage, the installation operated continually under one set of conditions, selected on the basis of results obtained during the first stage of the investigation; results of the second stage indicated that the process of nitrogen oxides absorption had to be based on a rationally (empirically) developed and controlled technological procedure. The first study stage extended over more than 1-1/2 months, and the second stage over more than 2-1/2 months. More than 3,000 analyses of the gaseous and liquid phases were made, which yielded sufficient experimental data for the determination of optimal technological conditions.

13415

Haseba, S., T. Shimone, N. Kubo, and T. Kitagawa

NITRIC OXIDE EXPLOSION. C. m. Eng. Progr., 62(4):92-96, April 1966. 8 refs.

A method was found to analyze low-concentration hydrocarbons assumed to have contributed to an explosion in the second heat exchanger of a nitrogen wash unit. Acetylene, 1,3-butadiene, and allene existed in the crude gas in the order of 2 to 3 ppm, 0.2 to 0.5 ppm, and 0.2 to 0.3 ppm, respectively. Nitric oxide was detected at concentrations in the order of 0.005 to 1 ppm through oxidation with permanganate and sulfuric acid, followed by calorimetric detection with the Griess-Saltzman reagent. Findings showed that more than 90% of NO entered the unit accumulated in the second heat exchanger, most of it oxidized to nitrogen dioxide and nitrous anhydride, which is more reactive with hydrocarbons than NO. Experiments confirmed the possibility of spontaneous ignition in the second exchanger and the composition of reaction products between nitrogen and conjugated dienes. An absorption process is now used to remove NO, in which Na2CrO2 or C12 are added to the wash-water circuit.

13481

Kirk, Donald G.

NITRIC ACID BLEACHING OF HARDWOOD NEUTRAL SULFITE SEMICHEMICAL PULP. Tappi, 51(4):145-151, April 1968. 26 refs. (Presented at the Fourth International Pulp Bleaching Conference jointly sponsore by the Technical Association of the Pulp and Paper Industry and the Technical Section, CPPA, held in Toronto, Ont., May 1-4, 1967.)

Use of nitric acid in place of chlorine as a first stage bleaching agent for a hardwood NSSC pulp has been studied. The purpose was the production of a high nitrogen effluent from which a fertilizer material might be recovered and marketed. Study of nitric acid stage variables showed the necessity of keeping the temperature low and bleaching duration short to prevent strength loss. This required the application of high nitric acid concentrations, which made reuse of the acid an economic necessity. Modifications using alcoholic nitric acid or nitric-sulfuric acid mixtures showed some potential strength benefits, while nitrous acid appeared to cause severe degradation. Extraction stage variables within broad limits were found to have little effect on pulp quality. Ammonia was found to have little effect on pulp quality. Ammonia was successfully substituted for caustic soda to increase the nitrogen content of the effluent solids. In general, substitution of nitric acid for chlorine in the first stage of a chlorine-extraction- hypochlorite sequence can be made to produce a pulp at least equivalent to the control pulp in all respects except for a slight yellowing effect. Chemical costs are high enough to render the process economically unattractive unless a fertilizer by-product can be marketed. (Author abstract)

13680

Atroshchenko, V. I., V. M. Kaur

KINETICS OF NITROGEN OXIDE ABSORPTION BY CONCENTRATED NITRIC ACID. (Kinetika pogloshcheniya okislov azota kontsentrirovannoy azotnoy kislotoy). Text in Russian. Zh. Prikl. Khim., vol.31: 352-360, 1958. 11 refs.

New experimental data regarding the kinetics of absorption of nitrogen oxides by concentrated nitric acid are presented. Dependencies between the absorption rate coefficient and basic physicochemical factors such as NO2 and N2O concentration in the gas phase, content of nitrogen oxides in the gas, HNO3 concentration in the acid, N2O4 content of the solution, and temperature are established. A dependence between absorption rate coefficients and basic hydrodynamic factors is demonstrated.

13948

Foerster, F., T. Burchardt, and E. Fricke

PRODUCTION OF CONCENTRATED NITRIC ACID FROM NITROUS GASES. PARTS A AND B. (Ueber die Gewinnung konzentrierter Salpetersaeure aus nitrosen Gasen). Text in German. Z. Angew. Chem. (Weinheim), vol. 1:113-117, May 11, 1920. PARTS C, D, AND E. Ibid., p. 129-132, May 25, 1920. 10 refs.

A detailed description and discussion is presented of two series of experiments on the formation of nitric acid from nitrous gases. In the first series, a mixture of gaseous nitrogen dioxide and oxygen was passed through a bell-type wash tower filled with a nitric acid solution. In the second series, oxygen was passed through a mixture of nitric acid and liquid nitrogen dioxide or else known amounts of oxygen and that mixture were thoroughly shaken together. Conclusions are as follows: 1. The notion derived from previous experiments that the process of nitric acid formation from gaseous NO2, O2, and water cannot proceed beyond the nitric acid solution with the lowest vapor pressure, is erroneous. 2. The rate of this process in the range of concentrations of nitric acid at the lowest vapor pressure is so low that an enrichment of nitric acid beyond this range requires a rather long reaction time. 3. For such an enrichment, the smallest possible excess of oxygen and a low rate of flow of the mixture are preferable. 4. With sufficiently long test durations and with progressively decreasing utilization of the NO2, even under the most favorable test conditions, nitric acid concentration rarely goes above 80%. 5. The reason for this is that when a steaming gas mixture is used, the conditions favoring a good utilization of NO2, namely, a small oxygen excess and low rate of flow, are highly unfavorable for the thorough mixing of the reaction solution with oxygen which is also required. 6. However, one can easily attain even the highest nitric acid concentrations if one mixes less concentrated solutions of it with an appropriate amount of liquid NO2 and shakes this mixture thoroughly with oxygen. 7. The process proceeds especially rapidly when the excess of liquid NO2 is so great that, due to its limited solubility in nitric acid, the liquid mixture is heterogeneous and remains so during the reaction. 8. When nitrous gases act on water, from the equilibrium 2NO2 yields N2O4, the latter is dissolved in water and yields the primary reaction N2O4 plus H2O yields HNO3 plus HNO2. 9. The dissociation of the nitrous acid into nitric acid, nitric oxide, and water (3HNO2 yields HNO3 plus 2NO plus H2O), and the rapid oxidation of the latter, effects the transformation of the nitrous gases into nitric acid up to its highest concentrations.

14303

Von Semel, Georg and Heinz Lehmann

METHOD OF PRODUCING CONCENTRATED MIXTURES OF NITRIC AND PHOSPHORIC ACID. (Pintsch Bamag A.-G., Berlin) U. S. Pat. 2,901,340. 2p., Aug. 25, 1959. 4 refs. (Appl. Dec. 26, 1956, 7 claims).

A method was devised for obtaining higher concentrations of mixtures of nitric and phosphoric acids by using a phosphoric acid solution instead of water. The method consists of passing a nitrogen oxide gas and an oxygen-containing gas into a dilute phosphoric acid solution with an inorganic nitrate or sulfate salt dissolved in it in an amount between 1% by weight and the solubility limit of the salt. The nitrogen oxide gas absorption is promoted by the inorganic salt which converts it to nitric acid. Thus, a concentrated solution of phosphoric and nitric acid is formed.

15087

Meszaros, Laszlo

THE PROCESS OF OXIDATION OF NITROGEN OXIDES IN THE PRESENCE OF EQUIMOLECULAR NO + NO2 ABSORPTION IN THE DILUTE TAIL GASES OF NITRIC-ACID PLANTS. (Nitrogenoxid oxidacioja hig nitrozus gazokban ekvimolekularis NO + NO2 folyamatos abszorpcioja mellett). Text in Hungarian. Magy. Kem. Folyoirat, 67(11):488-490, 1961. 1 ref.

A differential equation is derived that gives the incremental change in the partial pressure of nitrogen dioxide as a function of incremental change in nitric oxide concentration, oxygen concentration, the concentration of an inert gas, and the total pressure. The above conditions refer to the tail gas of a stack at a plant where nitric acid is manufactured from nitric oxide, sodium carbonate, and water; the tail gas (NO and NO2) concentration is 0.7-1.0 vol%. Subsequently, the equation is used to derive another differential equation rendering the time needed to accomplish an incremental change in NO concentration. This latter differential equation is considerably simplified so that it can be integrated. The resulting equation is presented in the form of a nomogram that can be used to calculate the volume of the absorber column or the oxygen concentration or the time needed to perform the reaction.

23882

Satterfield, Charles N. and Douglas H. Cortez

MASS TRANSFER CHARACTERISTICS OF WOVEN-WIRE SCREEN CATALYSTS. Preprint. Massachusetts Inst. of Tech., Cambridge, Dept. of Chemical Engineering. 38p., 1969 (?). 19 refs.

Gauze catalysts woven from a fine platinum-rhodium wire have long been used in the partial oxidation of ammonia for the industrial manufacture of nitric acid. An investigation of the possibility that the catalytic oxidation of hydrocarbons in air might under some circumstances proceed by initiation of reaction on a catalyst surface followed by propagation of the reaction into the surrounding gas, or so-called heterohomogeneous catalysis, is described. The rate of oxidation of benzene or toluene in excess air on platinum screen catalysts under mass transfer controlled conditions is used to calculate 'j' factors. Previous literature data on heat and mass transfer are re-examined and re-correlated and the transport characteristics of screen catalysts are shown to be very similar to that of infinite cylinders. There is no positive evidence that any of the hydrocarbon oxidation in these studies or that of the oxidation of ammonia on platinum gauze under industrial conditions occurs as a homogeneous process. (Author abstract modified)

G. EFFECTS-HUMAN HEALTH

01049

R. I. Larkin and R. F. Kupel

QUANTITATIVE ANALYSIS OF POLYVINYLPYRROLIDONE IN ATMOSPHERIC SAMPLES AND BIOLOGICAL TISSUES. Am. Ind. Hyg. Assoc. J. Vol. 26(6):558-61, Dec. 1965.

A quantitative method for the analysis of polyvinylpyrrolidone (PVP), collected in atmospheric samples or extracted from biological tissues, is described. PVP is a component in many aerosol hair sprays. A 0.4M citric acid solution is used to collect or extract the PVP. The color is developed by using a potassium iodide reagent, and the intensity of the color is read on a spectrophotometer at a wavelength of 432 millimicrons. The low limit of detection for this method has been established at 0.5 microgram of PVP per milliliter of final solution. (Author abstract)

08552

A. Goetz

AN INTERPRETATION OF THE SYNERGISTIC EFFECT OF AEROSOLS BASED UPON SPECIFIC SURFACE-ACTION OF THE AIRBORNE PARTICLES. Preprint. (1956).

Experiments to determine the survival time of test animals (mice) exposed to toxic vapor without and with the addition of an aerosol of defined particulate constitution were conducted. As toxic vapor, three different substances were used, (each for itself, i.e. not as mixtures): two aldehydes (formaldehyde and acrolein) and evaporated nitric acid; the concentration of these vapors was kept constant in the presence and absence of the aerosol addition, and it was selected so that the vapor alone caused communicatable survival periods of the animals. None of the aerosols caused, in the absence of the toxic vapors, any significant change in the test animals. However, when co-existent with the toxic vapors the aerosols caused very marked differences in the mean lifetime of the test animals and proved that certain types of particles produce a Substantial identification of the toxicity of the vapor (shortening of the lifetime), while others had an attenuating effect (lengthening of the lifetime), and also that the attenuating, or the intensifying properties of a particular aerosol, depended to a large extent on the nature of the toxic vapor. These investigators have attempted to interpret their results qualitatively (and to some extent even quantitatively) by assuming that the vapor be absorbed by the aerosol, i.e. by the gradual incorporation of the vapor into the particle. In view of the fact that the experimental data as well as the manner in which they were obtained, appear to have an unusually significant bearing upon the mucous irritation caused by smog, the present investigation has attempted to interpret this data in terms of nuclear condensation of the toxic vapor, (i.e. of a surface accumulation on the airborne particles).

11378

Meiekhina, V. P.

THE PROBLEM OF COMBINED ACTION OF THREE MINERAL ACIDS. In: Biological Effect and Hygienic Significance of Atmospheric Pollutants, Book 1/9, V. A. Ryazanov and M. S. Gol'dberg (eds.). Translated from Russian by B. S. Levine, U. S. S. R. Literature on Air Pollution and Related Occupational Diseases, Vol. 16, pp. 76-81, 1968. (6)) refs. CFSTI: PB 179141

The following concentrations of odor perception thresholds was established: 0.80 mg/cu m for sulfuric acid, and 0.40 mg/cu m for hydrochloric acid, corresponding H-ion equivalents are as follows: 0.01099, 0.01203, and 0.01053 mg/cu m. Any combination of 2 or 3 acids was clearly odor perceptible if the sum of their concentration fractions in corresponding relation to their individual threshold concentrations exceeded unity. Perceptible concentrations expressed in H-ions exceed the 0.01 mg/cu m level. Threshold reflex effect concentrations, as s.aded by eye adaptation to darkness, were on the level of threshold odor perception, or just above it. The reflex effect of nitric, sulfuric, and hydrochloric acids in atmospheric air of inhabited areas is a condition of H-ion concentration. The sanitary-hygienic condition of atmospheric air containing mineral acids can be reliably evaluated on the basis of H-ion concentration for the sum of the three acids under consideration as well as for each acid individually based on the H-ion index should not exceed 0.010 mg/cu m.

16460

Podgornova, N. S.

HEALTH PROBLEMS IN THE INSTRUCTION OF STUDENTS IN A CHEMICAL TECHNICAL SCHOOL. (Gigienicheskie voprosy obucheniya studentov khimicheskogo tekhnikuma). Text in Russian. Gigiena i Sanit., no. 9:112-114, 1966.

Psychological and physical studies were made of 85 students aged 15-18 years enrolled in three courses of study at the Moscow Chemical-Technological school during one semester. In Course I, students had 5 weeks of classroom work, 4 weeks of shop work, and then returned to classrooms for the remainder of the semester. Students in Course II had 6 hours of laboratory work one day a week in addition to daily classroom work. Students in Course III had classroom instruction all semester. At the end of the semester, all groups showed a decrease in work capability and physiological changes which were more marked in students in Courses I and II. No decrease in function was noted at the end of the day in students having shop or laboratory work. More control by the instructor is recommended in order to decrease fumes of nitric acid in laboratories.

16613

Prys-Roberts, C.

PRINCIPLES OF TREATMENT OF POISONING BY HIGHER OXIDES OF NITROGEN. Brit. J. Anaesthesia, vol. 39:432-439, May 1967. 39 refs.

The main methods of treatment for patients exposed to the noxious effects of nitric oxide, nitrogen dioxide, or the fumes of nitric acid are outlined. High concentrations of nitrogen oxides cause reflex inhibition of breathing with laryngospasm. In-

tense cyanosis develops rapidly. Therefore, severe hypoxia may occur. There is a tendency for the ventilatory frequency to increase, and pulmonary edema may occur in the acute phase. Oxygen therapy is recommended which consists of administering 100% oxygen, either by spontaneous or artificial ventilation in order to compensate for the decreased oxygen capacity and content of the arterial blood. Reconversion of methemoglobin by the use of methylene blue (2mg/kg) initially is advocated, with subsequent dosage titrated against the methemoglobin concentration in the blood. Prevention and treatment of chemical pneumonitis combines endobronchial and parenteral administration of corticosteroid preparations, together with bronchial lavage and suction. The metabolic component of acid-base derangement is corrected by intravenously administering sodium bicarbonate. Artificial ventilation by intermittent positive pressure ventilation may be indicated in patients who demonstrate ventilatory failure manifested by a rising arterial carbon dioxide pressure. Circulatory therapy is accomplished by the use of vasopressor agents to combat severe systemic hypotension. Associated drug therapy using dimercaprol is advocated in severe cases in view of the protective action of this type of agent against the higher nitrogen oxides. Bronchodilators may be indicated in order to alleviate bronchospasm arising from the irritant effects of the inhaled gases. (Author conclusions modified)

21307

Ellis, Richard E. and Ronald M. Bishop

OXIDES OF NITROGEN ARE HEALTH HAZARDS. J. Environ. Health, 32(6):676-677, May/June 1970. 4 refs.

Oxides of nitrogen are extremely toxic. Nitrogen dioxide and tetroxide are most prevalent. Both the threshold limit value and ceiling are 5 ppm and should never be exceeded. Occupational exposure is encountered in nitric acid manufacture, nitration of cellulose and inorganic materials, etching, pickling of metals, certain welding operations, explosives manufacture and use, and engine exhausts. The gas combines with water to form nitrous and nitric acid which, in turn, react with salts in the tissues of the respiratory tract to produce irritating nitrites and nitrates. Exposure to high concentrations may be fatal. Persons suspected of having been exposed should be kept under observation at rest for 25 hours. Persons known to have been exposed should be hospitalized at bed rest. Administration of oxygen and corticosteroids is indicated and may be life-saving.

23738

Gray, Edward Le B., Stanley B. Goldberg, and Francis M. Patton

TOXICITY OF THE OXIDES OF NITROGEN. III. EFFECT OF CHRONIC EXPOSURE TO LOW CONCENTRATIONS OF VAPORS FROM RED FUMING NITRIC ACID. Arch. Ind. Hyg., Occupational Med., vol. 10:423-425, 1954. 5 refs.

In contrast to animals exposed for four hours a day, five days a week for six weeks to 9-14 ppm nitrogen dioxide, rats, mice, and guinea pigs exposed for four hours daily, five days a week for six months to 4 ppm vapors of red fuming nitric acid exhibited no toxic effects. In fact, the lower concentration of NO_2 produced a significant prophylactic effect, since the degree of pulmonary congestion was less in the exposed animals than in control animals. The results lead to the conclusion that the maximum allowable concentration of nitrogen oxides should be set at 5 ppm.

24588

Gray, Edward LeB., James K. MacNamee, and Stanley E. Goldberg

TOXICITY OF NO2 VAPORS AT VERY LOW LEVELS. A PRELIMINARY REPORT. Arch. Ind. Hyg. Occupational Med., vol. 6:20-21, July 1952. 9 refs.

Forty rats were divided into groups of 10 and exposed to red fuming nitric acid containing 9-14 ppm nitrogen dioxide for four hrs at a time. Total exposure for the different groups ranged from 40-96 hrs. Animals examined shortly after the termination of exposure had inflammatory respiratory tracts and exhibited evidence of severe rhinitis and tracheitis in the upper portion of the tract, along with less severe pneumonitis. Pneumonia developed in a few of the animals. In many of the animals sacrificed eight or more weeks after exposure, the inflammation had subsided, but there were localized areas of emphysema in all lobes of the lungs. With the exception of moderate congestion, liver, spleen, kidney, and brain showed no pathological changes. Length of exposure had no effect on the changes observed. In view of the fact that nitrogen dioxide concentrations higher than 8 ppm produce damage in rats, it is concluded that the maximum allowable concentration of 25 ppm, the value set by the American Standards Association and others, is too high.

H. EFFECTS-PLANTS AND LIVESTOCK

22622

Neuck, Kurt

INVESTIGATIONS OF SMOKE GAS DAMAGES TO VEGETATION. (Untersuchungs uber die Rauchgasschaden der Vegetation). *Z. Angew. Chem. (Weinheim)*, vol. 42:123-126, Jan. 3, 1929. 6 refs. Translated from German. Bekov and Associates, Denver, Colo., 12p., May 27, 1976.

Investigations were conducted to determine if nitrous gas, hydrochloric acid, and ammonia cause plant damage similar to that caused by sulfur dioxide, and to determine the participation of the iron contained in chloroplasts in this disease process. The assimilation apparatus in the moss fontinalis was primarily affected by nitrous gas and these effects corresponded to the effect of SO2; HCl had a lesser effect, and ammonia was not considered to be an assimilation poison. Clover, tobacco, and spinach plants exposed to nitrous gas became withered and bleached with inhibited assimilation after exposure to light. Plant damage by SO2 and nitrous gas consists of a fixation of iron followed by a photooxidative poisoning of the protoplasm by chlorophyll. Tests on corn were conducted to determine if the water soluble part of iron increases after introducing assimilation poisons. Pre treatment with fuming nitric acid resulted in a water soluble iron content four times higher than normal. The effect of smoke gases on plants consists of a direct cancellation of the catalytic activity of the iron in the chloroplasts. The photooxidative poisoning of the protoplasm is considered to be a secondary effect.

25481

Clark, J. F.

ON THE TOXIC EFFECT OF DELETERIOUS AGENTS ON THE GERMINATION AND DEVELOPMENT OF CERTAIN FILAMENTOUS FUNGI. Botan. Gaz., 28(5): 289-404, Nov. 1899. 47 refs.

An experiment designed to determine the relative and absolute toxic properties of several chemical compounds, as shown by their influence on the spores, mycelium, and the fructification of certain of the mold fungi, is described. The procedures used to select the medium, the method of culture, and the experimental equipment and conditions are described. Cultures were examined at intervals of 3-6 hr for the 14 hr following their exposure to the various chemical agents, until the fungus had matured, or the spores in the cultures which had failed to germinate were transferred to pure beer infusion to test their vitality. The cultures in which the spores failed to germinate were divided into two classes; inhibited and killed. The cultures which did germinate were also divided into two groups; those which matured a fair crop of conidia in about the normal time and those which presented a markedly retarded mycelial development and generally failed to fruit. The types of chemical agents tested, in various strengths, include sulfuric, hydrocyanic, hydrochloric, nitric, and acetic acids, several metal sulfates, chromates, nitrates, and formaldehyde. The results indicate that fungi are generally more resistant than higher plants, although different species of fungi and different forms of the same species present considerable variation in resistance.

I. EFFECTS-MATERIALS

13877

McLeod, W. and R. R. Rogers

CORROSION OF METALS BY AQUEOUS SOLUTIONS OF THE ATMOSPHERIC POLLUTANT SULFUROUS ACID. Electrochem. Technol., 6(7 to 8): 231-235, July to Aug. 1968. 7 refs.

The corrosion rate of a metal in an acid with a normality between N/1 and N/10,000, such as H2SO3, HNO3, H2SO4, or HCL, was found to be related to the concentration of the acid in accordance with the equation Corrosion rate equals a x (Acid Normality) to the b power, where a and b are constant for each combination of acid and metal and where temperature = 25 C. By determining the values of a and b for a number of acid-metal combinations, it was possible to compare the corrosion rates of the various metals in sulfurous acid with those of the same metals in nitric, sulfuric, and hydrochloric acids, and to determine the corrosion rate of the metals in sulfurous acid of different normalities. Data obtained show that nonstainless steel, with or without nickel, is highly susceptible to sulfurous acid corrosion. However, when a substantial proportion of chromium is present in an alloy which contains nickel, steel is free from corrosion by either sulfurous acid or nitric acid. Copper and chromium are not appreciably susceptible to sulfurous acid corrosion in solutions lower than N/1.3. Tin corrodes more rapidly than other nonferrous metals between N/100 and N/1000, but less than cadmium and zinc at N/10. Cadmium, Lead, and zinc corrode more rapidly in sulfurous acid than in nitric acid. Lead corrodes less rapidly in sulfurous acid than in nitric acid. Aluminum is rapidly corroded by hyperchloric acid but less so by nitric or sulfurous acid. The study concludes that sulfurous acid solutions causing the greatest damage in urban and industrial areas have abnormalities between N/1 and N/10,000.

19325

Konda, Kiyoshi, Hisao Ito, and Atsuhiro Honda

FIELD EVALUATION OF EXHAUST GAS FROM REFUSE INCINERATOR RELATED TO AIR POLLUTION AND METAL CORROSION. Trans. Soc. Heating, Air-Conditioning, and Sanitary Engrs. (Japan), vol. 7:95-104, 1969.

A study of municipal incinerator exhaust gas composition conducted at five sites in Japan is described. The study was undertaken to obtain information on odor and metal corrosion problems. The exhaust consisted of sulfur oxides, nitrogen oxides, ammonia, sulfuric acid, nitric acid, organic acids, and hydrochloric acid. Volatile organic acids and hydrochloric acid are mainly responsible for the corrosion, with sulfuric and nitric acids only partially concerned. Percentages of exhaust products as a function of raw refuse input are tabulated. Continuous firing rather than batch firing would limit noxious effluents. Temperature and excess air control would also help. After-burning chambers should be installed to further reduce contaminants.

J. EFFECTS-ECONOMIC

17203

Oefs, Heinrich

AIR POLLUTION PROBLEMS IN WEST GERMANY AND THE ROLE OF INDUSTRY. (Luftforurensningsproblemer i Vest-Tyskland industriens innsats). Text in Norwegian. Tek. Ukeblad (Oslo), 116(45):1245-1247, Dec. 1969.

West Germany has been occupied in the last decade with reducing emissions of dust and smoke. Effectiveness of dust filters has increased threefold, and filtration is more economical. The dust content can now be reduced to 150 mg/cu m for an emission rate of 100,000 cu m/hr. In 1950, the dust output from the West German cement industry was 3.5% of the clinker produced; in 1967, it was 0.15%. Dust output from the manufacture of calcium carbide was reduced to 3 mg/cu m of exhaust gases. Attention now centers on reducing sulfur dioxide emissions. An electric power plant in Essen absorbs it with a new type of activated carbon, recovering the SO2 for the manufacture of H2SO4, the cost per 1000 kWh being about 1 DM (25 cents), and this can be further reduced. Government standards now limit the sulfur content of fuel oils to 1.8%. About 20% of the total SO2 emission in West Germany comes from sulfuric acid plants. A new 'double contact' process can reduce SO2 emissions of such a plant from 17 to 3 kg per ton of H2SO4 produced. Nitrogen oxides emitted from nitric acid plants have been reduced by 50% with special absorption equipment. New legislation sets a maximum average of 2 mg/cu m for fluorine emissions, or 5 mg for short intervals. Readings as high as 2.7 mg have been recorded above the Ruhr from January 1, 1966, to December 31, 1968. During that period, industry in North Rhine-Westphalia invested 4,000,000,000 DM on air pollution problems related to existent operations and about 275,000,000 DM on those related to new ones. Exhaust purification for the 2-year period cost 3,000,000,000 DM, plus an additional 30,000,000 for research this in comparison with a gross national product of 300,000,000,000 DM per year. The total amount spent by industry is small compared with the damage caused, which amounts to 50 DM per capita per year, or 3,000,000,000 for the entire republic, not including losses due to sickness or sanitation problems.

K. STANDARDS AND CRITERIA

05778

(INDUSTRY AND ATMOSPHERIC POLLUTION IN GREAT BRITAIN.) Industrie et pollution atmospherique en Grande Bretagne. Centre Interprofessionnel Technique d'Etudes de la Pollution Atmospherique, Paris, France. (1967.) 6 pp. Fr. (Rept. No. CI 310.) (C.I.T.E.P.A. Document No. 24.)

A summary of the basis of governmental action in Great Britain in the struggle against industrial emissions is outlined. The regulations imposed by the 'Alkali Act' are in most cases based on 'the most practical means.' Standards are given for chimney heights. Statutory limits are given for various materials emitted such as hydrochloric acid, sulfuric acid, nitric acid, hydrogen sulfide, chlorine, arsenic, antimony, cadmium, and lead. The construction of tall buildings tends to reduce the benefits obtained by tall chimneys. A better knowledge of the effects of pollutants should be obtained so as not to burden industry with unnecessary expense in their control. It is urged that international standards for emission be adopted.

07197

RECOMMENDATIONS FOR ALLOWABLE CONCENTRATION (1966.) Kuki Seijo (Clean Air - J. Japan Air Cleaning Assoc., Tokyo) 4(4):62-66, 1966. Text in Japanese.

A report is given by a committee of the Japanese Association of Industrial Health on 'Allowable concentration'. The values of allowable concentration are worked out for a healthy man working 8 hr per day doing moderate work. Proper consideration must be given to cases in which more than 8 hr of exposure take place, more than one pollutant is involved, or the concentration of pollutants increases suddenly during the work schedule. Included is a discussion on dust measurement. It is important to measure dusts having a Stokes radius of less than 5 microns, especially at a height of 1 to 1.5 m from the ground. The relation between the source of dust and the point of measurement is illustrated.

20121

RECOMMENDATIONS OF PERMISSIBLE CRITERIA OF HAZARDOUS WORKING ENVIRONMENTS BY JAPAN ASSOCIATION OF INDUSTRIAL HEALTH. 1969. Sangyo Igaku (Jap. J. Ind. Health), 12(2):37-44, Feb. 20, 1970. 15 refs.

The Japanese Association of Industrial Health annually recommends permissible concentrations of toxic gases, vapors, mist, and fumes in the working environment. The 1969 limit values for 88 toxic substances are shown in ppm and/or mg/cu m. Like the Threshold Limit Values established by the American Conference of Governmental Industrial Hygienists (ACGH), the concentrations are time-weighted average concentrations for an eight-hour working day. The table cannot be applied to works where exposure to toxic substances is extremely irregular or short-term. The limit values for butyl acetate, butyl alcohol, carbon monoxide, p-dichlorobenzene, ethylene glycol dinitrate, nitrobenzene, hexane, selenium compounds, lead, nitric acid, styrene monomer, toluene, 1,1,1-trichloroethane, and trichloroethylene differ from those of the ACGH. Factors affecting the Japanese decision are discussed in the case of hexane, lead, styrene monomer, and toluene. The article also reviews permissible criteria for noise exposure, thermal standards for high-temperature work, and permissible dust concentrations.

L. LEGAL AND ADMINISTRATIVE

05407

T. Tovama

AIR POLLUTION AND HEALTH IMPEDIMENT. Japan J. Ind. Health (Tokyo) 8, (3) 45-8, Mar. 1966. Jap. (Presented at the 39th Annual Meeting, Japan Society of Industrial Medicine, Ube, Japan, Apr. 7-9, 1966.)

The 39th Annual Meeting of the Japan Society of Industrial Medicine was held on April 7-9, 1966 in Ube, Yamaguchi-ken, Japan. The theme of one of the symposia was planning programs for air pollution control in which air pollution and health impairment and the engineering and practice of air pollution control were discussed. The main health impairments covered deal with effects of pollution on the respiratory system and acute diseases resulting therefrom. Prior to World War II there were no legal problems in pollution control but by 1963, it was necessary to establish laws covering soot and dust control. City planning and building restriction ordinances have come into effect. Dust and soot fall have decreased by one-sixth in the past sixteen years. Millions of dollars have been paid by factories and industries for the establishment of dust collectors and SO2 counter-measures. Waste gas disposal in nitric and sulfuric acid plants has been brought under control since 1964. Re-use of the waste gases has played an important role in the economic feasibility of air cleaning.

07597

Heller, A.

MAXIMUM PERMISSIBLE CONCENTRATIONS FOR AIR POLLUTION IN THE FEDERAL REPUBLIC OF GERMANY. Preprint, Federal Inst. of Hygiene for Water, Soil and Air, Berlin, Germany, 10p., 1963. (Presented at the Inter-Regional Symposium on Criteria for Air Quality and Methods of Measurement, Geneva, Switzerland, Aug. 6-12, 1963, Paper No. WHO/AP/IR.)

An advisory committee set up by the Federal Government gives expert advice on the proposals of the Clean Air Commission of the Association of German Engineers regarding permissible emissions as well as on the maximum concentrations of 'immissions' the MIK values - for various air pollutants. The task of the Verein Deutscher Ingenieure Commission is to set scientific and technical bases for appropriate air pollution control measures. The main task of the Commission is to draft recommendations for new technical regulations as a basis for the determination and control of air pollution, as follows: Minimum requirements regarding the concentration and precipitation of dusts and gases in the atmosphere, bases for calculating the distribution of dusts and gases and for determining the required height of chimneys, limits to the emission of dust and gas from sources of air pollution, and procedures for measuring dusts and gases. The provisions recommended for examining applications for licences to establish new plants or to alter existing plants are reviewed. Enforcement of these regulations will depend on the local situation, especially the existing pollution load. They will also depend on the extent to which further pollution could occur, without exceeding the tolerance limit or the MIK-value for the most sensitive among the reaction partners, whether human being, animal or plant, and on the technical processes of the industrial plant in question. In principle, all reasonable technical and economic possibilities for purifying waste gases should be exploited in equal fashion by similar industrial plants. Finally, industry should be prepared to bear more far-reaching demands regarding waste-gas removal, if a licence for a new industrial plant or for the extension of an existing plant is to be issued in an area already polluted. MIK-values have been set and are discussed for; sulfur dioxide, hydrogen sulfide, some nitrous gases and chlorine.

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